Enhanced Surface Protection By Electrophoretically Painted Epoxy Nanocomposite (EPP-ENC) Coatings

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Abstract:

The article highlights important features of a novel Electrophoretic painting (EPP) process of coating Epoxy Nano-composite (ENC) from an aqueous dispersion of an electro-activated epoxy polymer and a nano-clay (NC) like Montmorillonite (MMT), under the influence of DC electric field. A commercial grade bifunctional epoxy resin is transformed into a hydrophilic quaternary ammonium form through controlled amination and neutralisation. ENC coatings were electro-phoretically painted (EPP) on stainless steel and aluminium as cathode, followed by suitable curing. Their characterisation has shown significant enhancement in certain key properties with increase in MMT content up to 6% by weight of the polymer, viz. Cross Hatch Adhesion (CHA) showing Index 5B for no peeling, approx. 10 fold rise in electrical volume resistivity, approx. 2 fold rise in dielectric strength and enhanced corrosion resistance.

Surface Protection Effectiveness (SPE) was studied through measurement of loss in adhesion, coating weight and deterioration in dielectric properties of EPP-ENC coatings after exposure to 3.5% Salt Fog Test (SFT) in the corrosion test chamber for 15, 30 and 45 days as per the ASTM D-3359-87 method with respect to original values obtained before exposure to Salt Fog test. Values were also compared with those of the Conventionally brush-painted Epoxy Nanocomposite (CBP-ENC) coatings having same Epoxy-MMT composition and subjected to same exposure to SFT. EPP-ENC coatings having MMT content at 6-8% have shown the best corrosion resistance or SPE based on retention of Cross Hatch Adhesion (CHA), Coating weight and electrical volume resistivity and demonstrated using graphs.

Keywords : Electropainting; Nanocomposites; Electrophoretic; Epoxy Polymer

1. Introduction

Polymer Nano-Composites (PNC) based on nano-sized fillers dispersed in polymer matrices have been under study since more than a decade intended for various technological applications. The advent of synthesizing and characterising the nano-powders of metal oxides, layered silicate nanoclays like montmorillonite (MMT) and nano-carbons such as carbon nano tubes (CNTs) [1-3], have led to a paradigm shift in polymer composites technology. The conventional methods employed for their processing, particularly mixing of nano-filler particulates with the liquid polymer matrix generally using three-roll shear mixing technique have limitation [4] of restricted loading of nano-particulates due to rise in viscosity of the polymeric composition beyond processability, besides causing the agglomeration of nano-particles at higher loadings, consequently limiting the final functional properties of the resulting PNC. This limitation in the processing methodology still remains a challenge to researchers and needs to be addressed.

The electrophoretic deposition (EPD) of organic polymers like epoxy, acrylic, polyurethane, etc. has been reported [5-7] involving an aqueous emulsion bath which can be either anionic or cationic in nature obtained by suitable chemical modification of the polymer. The process has been used almost universally in industrial coating operations such as priming/electropainting of automobile car panels, electrical appliances, in biotechnology and several other commercial applications [8, 9].

In this article the author reports a novel electrophoretic painting (EPP) process for Epoxy Nanocomposite (ENC) coating on the surface of a metal substrate under the influence of d.c. electric field. Author also highlights the salient process parameters and characterisation of the cured ENC coatings for their physical, electrical and corrosion resistance properties.

2. Experimental

2.1 Materials:

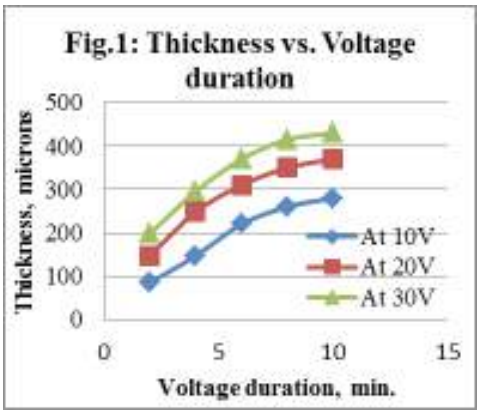
Solid Epoxy resin based on diglycidyl ether of bisphenol-A (DGEBA) with epoxy value in the range 1.0-1.2 eq./kg commercially available and without further purification was used for chemical modification into water dispersible form. Organic solvents like Ethylene glycol mono butyl ether, Methanol, Xylene and reagents such as primary and secondary amines and surfactant Triton X-100 of L.R. grade were procured from local market. Sodium Montmorillonite (MMT) nanoclay Cloisite Na+ from m/s Southern Clay Products, USA, was procured for use as nanoclay particles. Aluminium and Stainless steel sheets grade SI 304 of 1.75mm thickness cut to size 100 x 50 mm with edges rounded off, were used for cathode and anode during EPP process.

2.2 Methods used:

Extent of amination of the epoxy polymer was monitored by determining the epoxy equivalent using the standard volumetric method ISO 3001:1997(E) which is very sensitive and also by FTIR spectroscopic method by monitoring the reduction in the absorption band intensity of the epoxy group. Progress of electrodeposition of PNC film was monitored by drop in the current density and also by deposition-yield through weight and thickness measurements. Nanostructure of the deposited film was established using analytical techniques such as Scanning Electron Microscopy (SEM) and X-ray Diffractometry. Dielectric characterisation of electrodeposited PNCs was carried out by measuring the Breakdown voltage (BDV) by Dielectric strength tester and Volume resistivity was measured using Million Megohm meter.

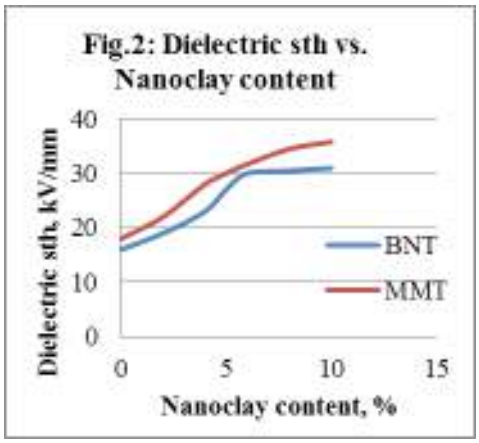
2.3 Amination of Epoxy resin and aqueous emulsion bath preparation:

DGEBA epoxy resin after dissolution in the polar solvent mixture containing methanol, butyl cellosolve and xylene was aminated at controlled temperature (65-70°C) and low-speed (40-50 rpm) stirring for about 4 hrs. Adduct is neutralised with acid resulting in an aqueous emulsion of quaternary ammonium salt. Nanoparticles of MMT or BNT are dispersed under ultrasonication at 20 kHz applied intermittently. The later helps intercalation of polycation in between the layers of the nanoclay platelets leading to exfoliation and thorough dispersion. Effect of MMT content from zero to 8% by weight of the polymer in the composition has been studied.



2.4 Electrophoretic painting (EPP) with Epoxy Nanocomposite (ENC) and Curing:

Electrophoretic painting (EPP) was carried out using an in-house fabricated plastic cell containing the formulation of aqueous epoxy emulsion prepared as above, equipped with two electrodes made from SS plates, a DC power supply and a magnetic stirrer to stir slowly the contents of the bath. ENC coating was electropainted on cathode by subjecting to DC electric field. Epoxy polycations together with MMT or BNT nanoparticles move towards the cathode plate and discharge on the metal surface forming the adherent layer of Epoxy nanocomposite (ENC) paint. Electropainted metal plate is removed from the bath, dried in air and cured at 150°C for 2 hrs in hot-air electric oven and subjected to characterisation.



2.5 Characterisation:

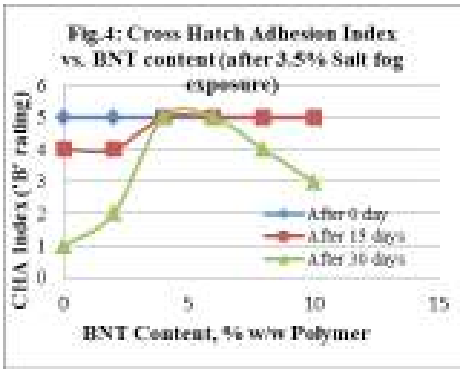
(i) Dielectric characterisation: EPP-ENC coating was subjected to measurement of AC breakdown voltage (BDV), dielectric strength and Volume resistivity. BDV is the puncture voltage of the cured ENC coating when alternating electric field is applied across the coating layer. Significant increase in the Dielectric strength is observed with increase in the nanoclay content from 0 to 6% as shown in fig.2.

(ii) Electrical volume resistivity and corrosion resistance: Retention of Electrical resistivity is used as the measure of corrosion resistance of ENC coating when exposed to corrosive environment such as 3.5% Salt-fog test for durations of 15 and 30 days as depicted in Fig.3.

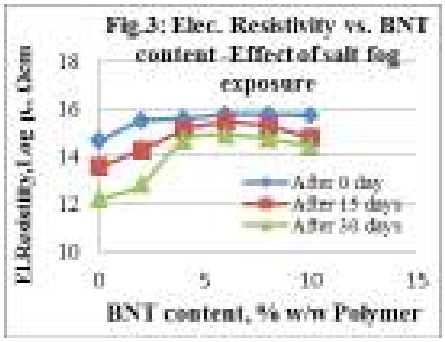
(iii) Adhesion test: ENC electropainted specimens were subjected to Cross Hatch Adhesion (CHA) Test and the retention of CHA Index values were considered as one of the criteria to indicate the resistance to corrosion against 3.5% Salt-fog exposure. ENC coatings containing different nanoclay content up to 6% by weight of the polymer have been characterised and depicted in Fig.4.

3. Results and Discussion:

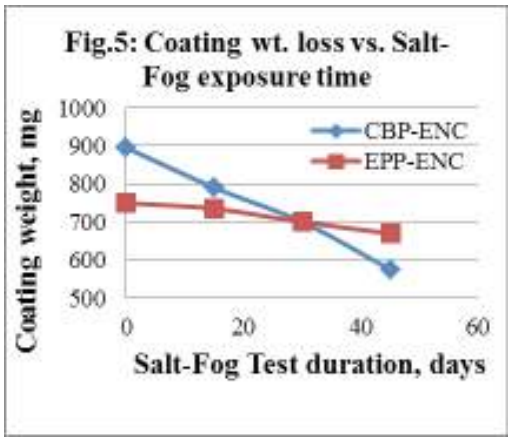
The data plotted in the fig.1 shows the positive influence of applied voltage and duration on the thickness build-up of the electropainted ENC coating. Rapid increase in thickness in the initial stages can be explained by higher electrical resistance exerted by the deposited coating and therefore the thickness is self-limiting.



Electrodeposition of ENC is also influenced positively by the increase in nanoclay content in the bath and may be explained as a consequence of good intercalation of polycations into the layered structure of the MMT and BNT nanoclay platelets. This phenomenon also explains the significant rise in the dielectric strength of the PNCs, almost 2-fold at the nanoclay loading levels of about 6-8 % by weight of the polymer matrix in both the cases as depicted in the Fig.2. It indicates great scope for EPP-ENC coatings for insulation application in HV machines.



Corrosion resistance, a significant property of the ENCs has been studied with respect to exposure period (0, 15 and 30 days) of Salt-Fog (3.5% NaCl) test, by measuring the electrical volume resistivity (considered as indicative of chemical resistance and structural integrity of the ENC coating) and the weight loss of the cured ENCs. A plot of logarithm of electrical resistivity (Log ñ‘ , &!cm) under above conditions versus BNT content as demonstrated in Fig.3 clearly shows lower Electrical resistivity values for ENC coatings which are exposed to longer duration of SFT test, while better retention of Volume resistivity or corrosion resistance can be noticed at shorter exposures to SFT.



Retention of adhesion of ENC coatings represented by CHA Index values as shown in fig.4, is at its best when the BNT content is in the range 6-8% by weight of epoxy matrix even after 15 and 30 days of exposure to SFT. Retention of weight of ENC coatings after exposure to SFT also indicates the corrosion resistance as shown in Fig.5. Conventionally brush painted (CBP) ENC coatings have shown greater weight loss during SFT test (for 15, 30 and 45 days exposure) as compared to electrophoretically painted (EPP) ENC coatings. These experiments have demonstrated the superiority of EPP-ENC coatings in Corrosion Resistance as compared to CBP-ENC coatings.

4. Conclusion:

Commercial epoxy resin DGEBA type was successfully modified into a water dispersible electroactive cationic polymer. A novel process for electrophoretic painting (EPP) of epoxy nanocomposite (ENC) containing a montmorillonite and Bentonite nanoclay has been established. Dielectric strength of neat epoxy EPP coating at 18kV/mm rises to about 35kV/mm at 6% MMT content. Similarly, Volume resistivity of EPP neat epoxy at 4 x 10^{15} Ùcm rises to 43 x 10^{15} Ùcm at 6% MMT content, indicating its suitability for electrical insulation application. EPP-ENC coatings have shown superior Corrosion resistance at 6-8% of Nanoclay content in terms of retention of Volume resistivity, Cross Hatch Adhesion Index and also lower weight loss as compared to CBP-ENC coatings when measured after 15, 30 and 45 days exposure to Salt-fog test.

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