

ELECTRODEPOSITED ORGANIC-INORGANIC NANO-COMPOSITES (EOINCS) – HIGHLIGHTS OF PROCESSING, APPLICATION AND FUTURE SCOPE

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Abstract : In this article, the author reports a new class of Organic-inorganic Nano-composites (OINCs) prepared by electrophoretic codeposition (EPD) of electro-activated organic polymer matrix together with the inorganic nano- particles under the influence of dc electric field, followed by appropriate curing. The process utilises a commercial grade bifunctional epoxide polymer duly electro-activated and converted into an aqueous emulsion in which the nanoclay particulates (NP) of Montmorillonite (MMT) and Bentonite (BNT) are dispersed and ultrasonicated. The novel process permits the higher NP content beyond 8% by weight of the polymer in aqueous bath. EPD process parameters like, bath composition, applied voltage, time and electrode spacing, have been studied. The author highlights some results in one of the studies [7] showing significant improvement in physico-mechanical and dielectric properties, viz., adhesion (no peeling as per ASTM D-3359-87), corrosion resistance (after 800 h. exposure to 4% salt fog), increase in dielectric strength by about 2 times (36kV/mm), volume resistivity by 10 times ($4.3 \times 10^{16} \Omega\text{cm}$) at 8% by weight MMT loading, as compared to the pristine polymer.

Index Terms : Epoxy, Electrophoretic, Nanocomposite, Electrodeposition.

I. INTRODUCTION

Polymer Nano-composites (PNCs) containing inorganic nano-particles have been under investigation by researchers world over due to their enhanced physico-mechanical and electrical properties over their pristine and conventional counterparts [1-3]. Range of PNCs based on epoxy matrix have been recently reported [2-4] incorporating specific nano-fillers e.g., nanoclays, metal-oxides, graphite, carbon nano tubes (CNT), iron oxide etc., resulting in a variety of corresponding nano-composites with insulating, semi-conducting or magnetic properties. Such semi-conducting PNCs containing CNTs have been reported [3, 5] for Electromagnetic Interference Shielding Effectiveness (EMI-SE) in electronic equipments. Recent advent of inherently Conductive Polymers (ICPs) viz., Polyaniline, Polypyrrole, Polythiophene etc. [6] in combination with conductive nano-fillers have led to another class of PNCs having enhanced electrical conductivity.

Conventional PNCs are applied on the substrate surface by traditional techniques like spraying, brushing, rolling or dipping to obtain a layer of desired thickness followed by suitable curing regime. However, such methods employed for their processing have the limitation [4-6, 8] of restricted loading of nano-particulates due to rise in viscosity of the polymeric composition beyond processability, besides causing 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 [7, 9-12] involving an aqueous emulsion (anionic or cationic) obtained by suitable chemical modification of the polymer. The process has been used frequently in industrial coating operations such as priming/ electro-painting of automobile car panels, electrical appliances, in biotechnology and several other commercial applications.

In this article the authors report a novel electrophoretic deposition (EPD) process for synthesis of PNC coating on the surface of a metal substrate under the influence of d.c. electric field. Authors also highlight the salient process parameters and characterisation of the cured PNC coatings for their physico-mechanical, dielectric and anti-corrosion properties.

II. EXPERIMENTAL

2.1 MATERIALS USED

Commercially available grade of Epoxide resin based on diglycidyl ether of bisphenol-A (DGEBA) in conjunction with customized mixtures of laboratory reagent grade primary and secondary amines and organic solvents like Ethylene glycol mono butyl ether, Methanol and Xylene available from SD Fine Chemicals were used in the chemical modification and electroactivation of the base epoxy polymer. Sodium Montmorillonite (MMT) nanoclay Cloisite Na⁺ and organically modified MMT (OMMT) from m/s Southern Clay Products, and Bentonite (BNT) from Sigma-Aldrich was used as inorganic 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 electrophoretic deposition (EPD) process.

2.2 METHODS USED

The extent of amination of epoxy polymer was monitored by epoxy equivalent determination using the standard volumetric method ISO 3001:1997(E) and also by FTIR spectroscopy. Progress of EPD of PNC coating 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 Scanning Electron Microscopy (SEM) and X-ray Diffractometry. Dielectric characterisation of EPD-PNCs was carried out by measuring the Dielectric strength using the Breakdown voltage (BDV) tester and Electrical volume resistivity was measured using Million Megohm meter.

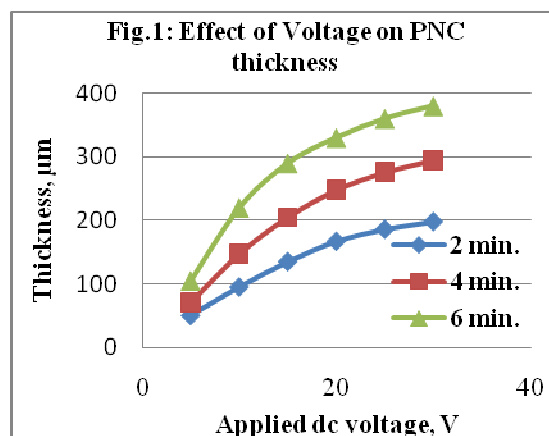
2.3 AQUEOUS DISPERSION OF EPOXY POLYMER MATRIX

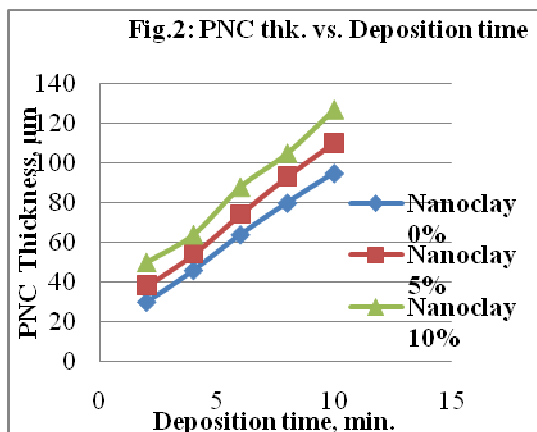
Epoxy resin is chemically modified through controlled amination followed by acidification to obtain the quaternary ammonium salt. It is dispersed in water to form a cationic epoxy emulsion as described in our earlier publications [7]. The MMT nano-particles were dispersed under ultrasonication at 20 kHz to facilitate the intercalation of polycations in between the layers of the nanoclay platelets leading to exfoliation of the particles and thorough dispersion. Nano-compositions with NP content varying from 0 to 10% by weight of the polymer were obtained.

2.4 ELECTROPHORETIC DEPOSITION (EPD) OF PNCs:

An in-house fabricated lab-scale EPD Cell was used containing the aqueous electroactive epoxy bath formulation prepared as above, equipped with two SS or Al plates acting as cathode and anode, a DC power supply and a magnetic stirrer to stir continuously and gently the contents of the bath. Application of suitable DC voltage to the electrodes results in the movement of the polycations together with nanoclay particles and codeposition on the cathode plate forming the adherent layer of polymer nanocomposite (PNC). The cathode metal plate electrocoated with PNC is removed from the EPD bath, dried in air and cured at 150°C for 2 hrs in hot-air electric oven and subjected to characterisation.

2.5 CHARACTERISATION





2.5.1 Controlling the Amination of Epoxy Polymer:

The extent of amination of epoxy polymer was monitored using the Standard Volumetric Method as per ISO 3001:1997(E) for Epoxy Equivalent Determination. The method is fairly sensitive. The epoxy-equivalent of the prepared epoxy-amine adduct was found to be in the range 2600-2700 g/eq against the initial value in range 850-900 g/eq as measured by above method, indicating the loss of epoxy groups of the polymer molecule during amination process.

2.5.2 FTIR Spectroscopy :

Infrared spectra of epoxy polymer and its amine-adduct were recorded using KBr pellet medium. Comparison of the two confirms the epoxy-amine adduct formation. IR spectrum of Epoxy polymer

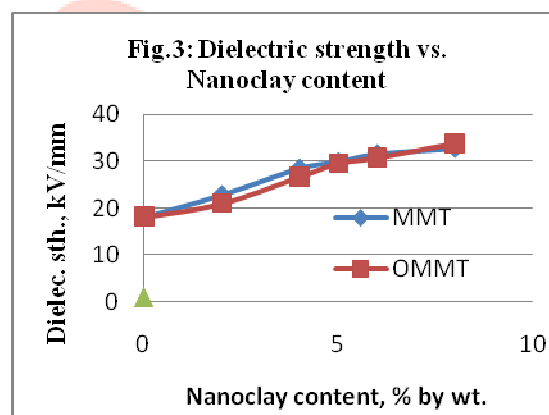
shows the typical band at 914 cm^{-1} due to the terminal epoxy group confirmed by the presence of band at 1245 cm^{-1} and the same is very weak in the spectra of the adduct besides the sharp bands at 1361 and 1379 cm^{-1} indicating the presence of tertiary amino group in the adduct. The results have been discussed in our earlier publication [7].

2.5.3 Monitoring the EPD process: The Electrophoretic deposition (EPD) process was monitored through the process parameters, namely, voltage, time, electrode spacing, bath composition, resin and nanofiller content, etc. that influence the quality of the electrodeposited coating. Only the important ones such as effect of voltage, time and nanoclay content are respectively shown in fig.1 and 2 and discussed in subsequent sections.

2.5.4 Dielectric characterisation: Dielectric characterisation of the cured EPD-PNC coatings with different MMT nanoclay content by weight of polymer, was carried out by measuring the Dielectric strength and Volume resistivity, using "Microdyne" BDV Tester and a Million Mega-ohm Meter respectively. The results are depicted in Fig.3 and Fig.4 respectively.

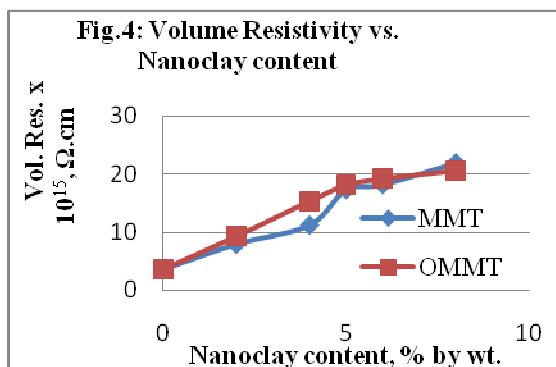
2.5.5 Corrosion Resistance of PNCs:

Electrodeposited PNCs having 5 different compositions with nanoclay content at 2, 4, 6, 8 and 10% by weight of epoxy each based on three different nanoclays viz. MMT, OMMT and BNT were subjected to Salt Fog Test with 4% NaCl concentration for the duration of 400 and 800 hrs. Exposed PNC coating specimens were removed from the chamber, dried and examined for their Cross Hatch Adhesion (CHA) strength tested as per the standard ASTM D3359-87 method. The corrosion resistance is assessed by retention of cross hatch adhesion (CHA) strength Index of the film against the surface of the substrate and is shown in Fig.5.



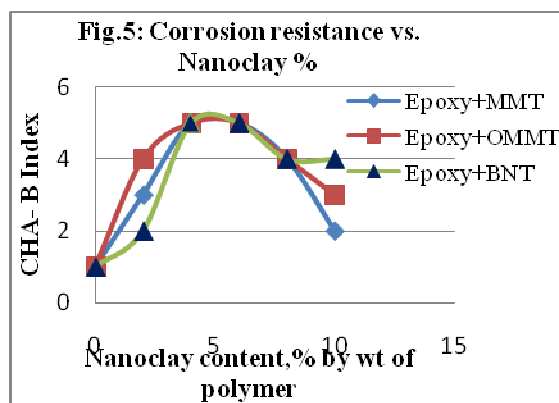
III. RESULTS AND DISCUSSION

Impact of increase in applied dc voltage from 5V to 30V on the thickness build-up or deposition yield of the EPD-PNCs is shown in Fig.1 with duration of deposition being 2, 4, and 6 minutes. It can be noted that thickness build-up is fast in the beginning but becomes sluggish after about 6 minutes in each case. This happens



due to inherent resistance or the insulation characteristic of the deposited nanocomposite coating. Fig.2 shows the increase in the deposited thickness with deposition time at a constant voltage of 10V at the nanoclay content of 0, 5 and 10% by weight of the polymer. This confirms the direct dependence of EPD-PNC on the applied potential and the deposition time

Dielectric characterization plots as shown in fig.3 and fig.4 pertaining to Dielectric strength and Volume resistivity respectively of the EPD-PNC coatings show significant improvement with increase in the MMT and OMMT content. Dielectric strength of neat epoxy EPD coating at 18 kV/mm in the beginning, rises to about 36kV/mm at 8% MMT content as shown in fig.3. Similarly, the initial Volume resistivity of neat epoxy at $4 \times 10^{15} \Omega \text{ cm}$ rises to $4.3 \times 10^{16} \Omega \text{ cm}$ in fig.4. This indicates that EPD-PNC nanocomposite coatings are much superior in their electrical insulation performance than their pristine epoxy counterpart.



Plots of Cross Hatch Adhesion (CHA) Index shown in Fig.5 for 3 different EPD-PNCs based on different nanoclays viz. MMT, OMMT and BNT clearly demonstrate that the best corrosion resistance is observed at the 4-6% by wt. of nanoclay, as the Cross Hatch Adhesion of EPD-PNC coatings is highest in this range.

The above results demonstrate two important functions of these EPD-PNC nanocomposites, one as Dielectric insulation, and the other is Corrosion resistance when the nanoclays like MMT, OMMT and BNT are used as inorganic nanofiller.

IV. FUTURE SCOPE OF THE EPD PROCESS

Further studies are in progress to extend this EPD process to electrodeposit semi-conducting and conducting PNCs containing the conducting nano particles like, nano-ferrites, CNTs, graphenes, and their hybrid combinations dispersed in the same host epoxy matrix, targeted for EMI shielding of electronic devices including the strategic aircraft systems. The EPD process has the advantage of permitting higher loadings of the nanophase particles in the polymer matrix in aqueous medium (viscosity not an issue) resulting in superior functional properties, besides being eco-friendly (clean and green) and economical. In summary, in this paper, the author has attempted to showcase the novel Electro-phoretic deposition process to produce functional PNCs that could turn out to be one of the futuristic processes for versatile applications.

V. CONCLUSION

Organic polymer matrix based on DGEBA epoxy was successfully electroactivated and converted into an aqueous cationic emulsion. Novel method for electrophoretic deposition (EPD) of an organo-inorganic nanocomposite (OINC) containing the nanoclays like MMT, OMMT and BNT dispersed in epoxy polymer matrix has been established. Incorporation of about 6-8% nanoclay by weight of the epoxy polymer in the formulation resulted in significant improvement in the dielectric strength of EPD epoxy nanocomposite coatings by about 2 times up to about 36 kV/mm. Similarly, in the same nanocomposite the Volume resistivity rises to approx. $4.3 \times 10^{16} \Omega \text{ cm}$, about 10 fold increase with respect to that of the pristine EPD-epoxy coating. This indicates its suitability for HV electric insulation application. As Corrosion resistant functional coatings the EPD-PNCs show high Cross Hatch Adhesion Strength with CHA-Index 5B and retains the same even after 800 hr. exposure to Salt Fog Testing as per the ASTM standard. The EPD process is universal in nature and can be extendable to co-deposition of semiconducting nanoparticles like CNTs, Ferrites and an electroactive polymer matrix to fabricate a new class of electrodeposited Polymer nano-composites (EPNCs) on a variety of substrates including FRPs suitable for industrial, electronics and aerospace applications.

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