A Novel Method in the Processing of Epoxy Nanocomposites by Electrophoretic Deposition

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Abstract

Polymer nanocomposites (PNCs) constitute a new class of advanced materials having uniquely enhanced physico-mechanical properties. They are important polymer matrices into which, dispersed inorganic nanoparticles like metal oxides viz. Titania, alumina or nanoclays (montmorillonites) etc. are conventionally added. epoxy based nanocomposites (ENCs) are prepared by incorporating the nanofillers or nanoclays into the liquid epoxy matrix by mechanical dispersion using ultrasonication, followed by solidification using suitable curing agent. Ultrasonication is adopted to cause intercalation of polymer molecules in between the lamellar layers of the montmorillonite clay platelets leading to exfoliation and effective dispersion of the nanoparticles in the resin matrix.

This paper presents a novel electrophoretic deposition (EPD) method for preparation of nanocomposites. The process involves the conversion of a bifunctional epoxy resin into a water dispersible polyelectrolyte emulsion via an amine adduct formation, dispersion of inorganic nano particles, and eventually electrodepositing the nanocomposite as a coating onto a metal substrate under the influence of DC voltage. The paper highlights the Chemical (FTIR), morphological (SEM), and thermal analysis (TGA) characterisation techniques used in these studies, along with some preliminary results on uniformity of nanoparticle dispersion, coating thickness and certain process parameters etc.

Keywords: *nanoclays, montmorillonite, nanocomposites, electrophoretic deposition, SEM, FTIR ,TGA.*

1. Introduction

Polymer nanocomposites (PNCs) have been attracting the focus of researchers for over a decade. PNCs generally contain an inorganic nano-filler such as metal oxide, silicate or a nanoclay. Such nano composites prepared by incorporating nano-sized inorganic filler particulate in the polymer matrix at as low loading volumes as <7 percent by weight, have been reported [1-6] to possess enhanced physico mechanical and dielectric properties. However, the higher contents of nanoscale fillers in the nanocomposites do not exhibit further improvement in the properties [6].

Natural montmorillonite nanoclays, have lamellar structure comprising of a layer of alumina

octahedrons, surrounded by two layers of silica tetrahedrons [7]. The residual negative charge in the layer is compensated by the cation present in the interlayer spacing. The exchange of these cations by that of the intercalating agent or polymer results in the higher compatibility of the montmorillonite with the polymer. On treatment with liquid polymer or intercalating agent the layered nanoclay initially undergoes intercalation and finally exfoliation.

PNCs are prepared by dispersing the nano filler in the liquid polymer using ultrasonication, followed by conventional processing, having enhanced physico mechanical and electrical properties. For example, Transmission Electron Microscopy (TEM) and the wide-angle X-ray diffractometry (WAXD) of Epoxy nanocomposites [9] containing α-Zirconium Phosphate nanoplatelets, have confirmed that the level of nanoplatelet exfoliation could strongly influence mechanical properties and the fracture mechanisms of the polymer nanocomposites. Similarly, Epoxy nanocomposites [10] containing 5% TiO2 nanoparticles have shown improved resistance to surface erosion by partial discharge (PD) attack studied by using a mechanical surface profilometer and a scanning electron microscope. The Erosion depth and the surface roughness were reported bo be far smaller in the specimens with nanofillers than those without nanofillers.

The problem of compatibility between the organic-inorganic interfaces, was addressed by using the organically modified nanoclay or organoclay [11]. An epoxy-silicate nanocomposite prepared by dispersing the organoclay into a liquid DGEBA epoxy resin and curing with either anhydride and/or amine hardener, has shown a good wetting of the silicate surface by the epoxy matrix and a good dispersion of the layered silicate having smectite layer spacings of 100°A or more within the crosslinked epoxy matrix. X-ray diffraction and Atomic Force Microscopy have shown better dispersion of Alkyl ammonium ion modified montmorillonite (MMT) in an Epoxy/Methyl nadic anhydride (MNA) based Epoxy nanocomposites [12] and improvement in their impact strength by about 12.4% with respect to pure epoxy.

Recently, a new class of polymer nanocomposites containing nanosized inorganic filler particles in the polyelectrolyte matrix prepared by electrophoretic deposition (EPD) process, have been reported [13-18]. EPD Process is a novel method to deposit composite films containing inorganic nanoparticles

and a polyelectrolyte under the influence of a DC voltage. The process involves dispersion of cationic or anionic polyelectrolyte in water and charged nanoclay or nanofiller particles and their electrophoretic movement towards the respective electrodes and subsequent deposition. Various inorganic materials such as metal oxides, hydroxides, silicates, carbonates, nitrides, carbides, borides, metals, alloys etc. in combination with polymers can be electrophoretically deposited on conductive substrates [19, 20].

Nanocomposite coatings based on polyelectrolytes like Poly(diallyl dimethyl ammonium chloride)(PDDA), using the method of electrophoretic codeposition of PDDA and cathodic electrosynthesis of metal oxides and hydroxides of Zr, Ce [14], Ni and Co [15] were reported involving the study of deposition mechanism, kinetics of deposition, microstructure and composition of nanocomposite films as well as the control of composition and quantity through process variables e.g. current density, deposition time and PDDA concentration in solution.

Several papers and patents are available in literature [21-26] describing methods of preparation of electrodepositable epoxy based aqueous compositions containing conventional fillers, their electrophoretic deposition and study of electrodeposited coatings. Kaylo Alan J., et. al. in their patent reported [27] the Cationic electrodepositable compositions comprised of an acidified aqueous dispersion of a cationic epoxy resin, a curing agent, and an exfoliated silicate derived from a layered silicate, and the method of electrocoating on conductive substrates. They showed that these compositions exhibited improved crater control.

Recently a composite epoxy coating containing montmorillonite obtained by an electrophoretic deposition (EPD) process has been reported [28]. The microstructural analysis TEM and XRD confirmed the intercalation of montmorillonite layers with epoxy. Functional characterisation (EIS and TMA) demonstrated the improved properties of the reinforced epoxy coating with respect to the simple epoxy coating.

2. Materials and Methods

Commercial Epoxy resin based on diglycidyl ether of bisphenol-A (DGEBA) from m/s Atul Ltd. with

epoxy equivalent weight of 833-895, Laboratory reagent grade amines such as n-Butyl amine and Diethyl amine from SD Fine Chemicals and Urea and formaldehyde of m/s Thomas baker make were used in the preparations. Ethylene glycol mono butyl ether, Methanol and Xylene of Laboratory reagent grade were used as solvent during the preparation.

Sodium Montmorillonite nanoclay Cloisite Na+ from m/s Southern Clay products, USA, was procured for use as nano-filler particles. Stainless steel sheets grade SI 304 of 1.5mm thickness cut to sizes 100 x 25 mm and 100 x 50 mm with edges rounded off, were used for cathode and anode during EPD process.

2.1 Preparation Of Aqueous Cationic Epoxy Emlsion:

In order to make epoxy resin water dispersible it is necessary to introduce an ionisable group, a quaternary ammonium group in its molecular structure for making a cationic resin. A solution of DGEBA epoxy resin is treated with a secondary amine while stirring and allowed to react under controlled reaction conditions to form an Epoxy-amine adduct. The solutions of epoxy-amine adduct and a lab made aminoaldehyde resin are mixed and acidified to form a quaternary ammonium salt. The product thus formed is dispersed in water with continuous stirring to form an emulsion, that is found to be reasonably stable at room temperature for long duration, without any separation from water or lump formation.

The montmorillonite nanoclay Cloisite Na+ particles is dispersed using ultrasonication at 20kHz. The ultrasonication process helps the intercalation of polyelectrolyte cation between the layers of the nanoclay platelets leading to exfoliation of the particles and thorough dispersion.

2.2 Study of EPD Process Parameters:

Montmorillonite nanoclay Cloisite Na+ was dispersed in the cationic epoxy emulsion by subjecting to ultrasonication at about 20 kHz frequency. The resulting dispersion of nanoclay was very stable without any separation or agglomeration of nanoparticles for prolonged periods, storable for several weeks, indicating effective intercalation and exfoliation of the nanoclay platelets. An electrophoretic cell comprising of a cathode and an anode connected to a DC source was fabricated. Electrodeposition of epoxy nanocomposite at different dc voltages was carried out on stainless

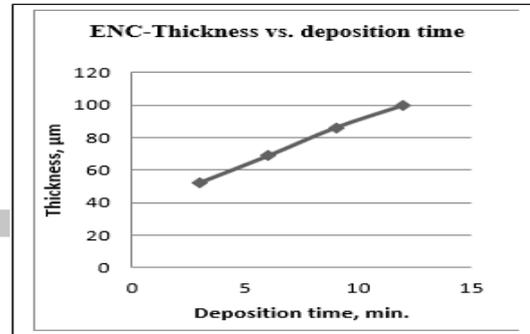steel plate specimens of size 100 x 25 or 50 mm, followed by drying and curing.

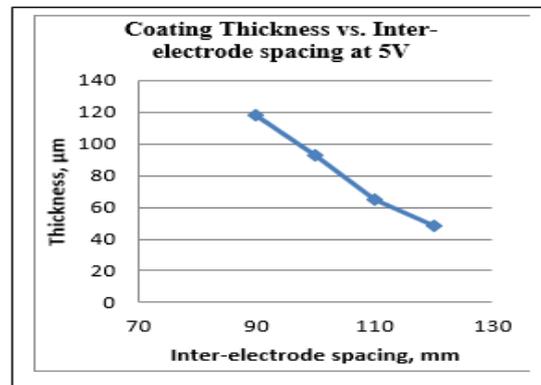

Fig1: ENC thickness vs, deposition time at 5V

Fig.2: Coating thickness vs. inter-electrode spacing

For comparison, EPD of neat epoxy coating, without nanoclay particles, was also carried out and coatings were cured under the same condition. Quality of deposited coating, like uniformity, freedom from defects such as blisters, cracks or peeling off, was critically observed. Coating build-up with respect to deposition time (Fig.1), was monitored by thickness measurement using "INSPEX" digital coating thickness gauge.

To avoid gassing on the electrodes and to obtain the uniform and defect-free coating, the applied voltage was kept low, below 30V and the distance between the electrodes is varied while keeping all other parameters constant. Fig.2 shows the decrease in the thickness build-up with respect to increase in the inter electrode spacing.

2.3 Curing of Nanocomposite Coating:

Extent of cure of coating was ascertained by determining the insoluble Gel Content using the Soxhlet Extraction method using acetone as solvent. The percentage of insoluble matter or the extent of cure at 150°C for different durations has been determined and plotted in fig.1. Optimum cure schedule is established as the insoluble or cured

polymer content approach almost constant (96-97%) after 3 hrs at 150°C.

3 Characterisation:

3.1 Epoxy Equivalent Determination:

Standard Volumetric Method as per ISO 3001:1997(E) for Determination of Epoxy Equivalent was used to monitor the epoxy-amine adduct formation. The method is fairly sensitive and the results are shown in the Table no. 1.

Table 1: Determination of Epoxy Equivalent of Epoxy resin and Adduct

Sl. no.	Resin	Ep. Equiv.(g/eq) (datasheet)	Ep. equiv. (g/eq) (measured)	Test method
1	Epoxy resin	833-895	901-933	ISO 3001:1997(E)
2	Epoxy-amine adduct	-	2836-2882	- do -

3.2 FTIR Spectroscopy:

FTIR spectra of epoxy resin and epoxy amine adduct were taken on Perkin Elmer FTIR "Spectrum-BX" Spectrophotometer using KBr pellet medium at I.I.Sc., to confirm the epoxy-adduct formation by comparison [8] .
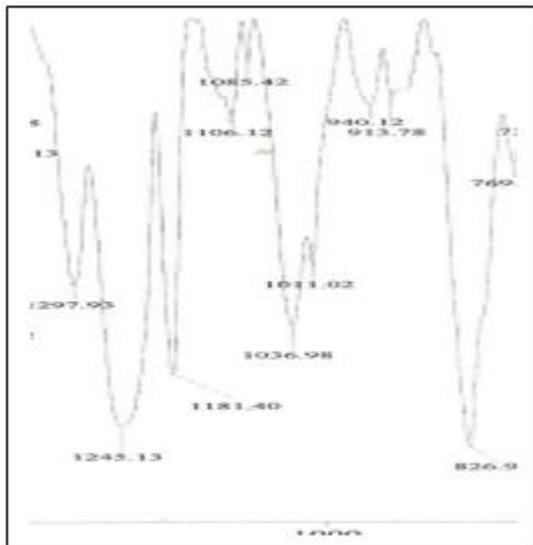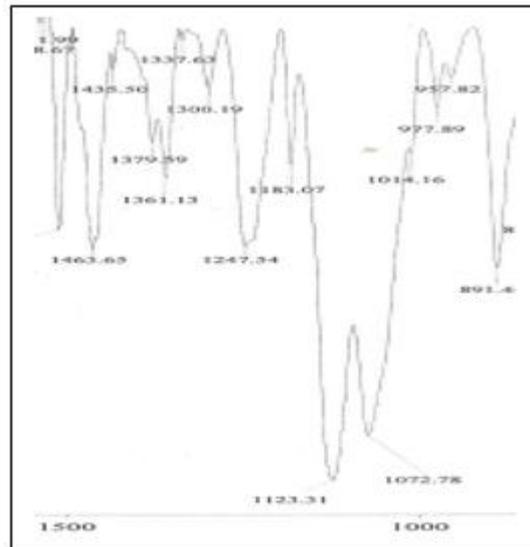
Fig.3. FTIR spectrum of Epoxy resin

Fig.4. FTIR spectrum of adduct

IR spectrum of Epoxy resin (fig.3) shows the typical band at 914 cm-1 due to the terminal epoxy group confirmed by the presence of band at 1245 cm-1 besides the presence of other groups of a DGEBA epoxy resin.

IR spectrum of Epoxy adduct (fig.4) shows the absence of typical absorption band of epoxy group at 914 cm-1 indicating the consumption of epoxy groups in adduct formation. The sharp bands at 1361 and 1379 cm-1 indicate presence of tertiary amino group of the epoxy-amine adduct.

3.3 Thermogravimetric Analysis (TGA):

TGA was conducted at Thermogravimetric Analyser Model V4.3A of TA Instruments at CPRI. The sample of EPD epoxy nanocomposite coating was subjected to TGA in air to check the thermal stability of the coating. The thermogram is shown in Fig.6. The coating is fairly stable upto 175°C when the weight loss or decomposition begins.

3.3: MECHANICAL PROPERTIES:ADHESION STRNGTH AND TENSILE STRENGTH

Adhesion strength rating of the EPD coating of neat epoxy and the nanocomposite containing 4% MMT by weight of the resin given in Table

Sl. no.	SUBST RATE	EPD Coating	Nanoclay content	C.H.A Rating
1	Al	Neat Epoxy	0	4.5B
2	Al	Ep + MMT	4%	5B

Standard method D638 was used for the determination of the tensile strength of the pure epoxy resin and MMT-Epoxy nanocomposite. using Universal Testing Machine. The results are given in table

Sl. no.	SUBST RATE	EPD Coating	Tensile strength N/mm^2	Breaking Force
1	Al	Neat Epoxy	13.6	528.2
2	Al	Ep + MMT(4%)	14.5	586.4

4. Results and Discussion:

It may be noted from section 2.3 that we have successfully developed an electro-active and stable aqueous emulsion based on cationic epoxy resin system which facilitates cathodic deposition of epoxy resin and the dispersed nano filler particles. Formation of epoxy-amine adduct was monitored by determining the epoxy equivalent of the adduct and comparing with that of the epoxy resin as shown in the Table 1. This is confirmed by FTIR spectra of the two products respectively as given in Fig.3 and Fig.4 wherein the spectrum of the adduct shows the loss of terminal epoxy group and the appearance of tertiary nitrogen group in the molecule as reported in the section 3.2.

Curing schedule for the EPD-ENC has been optimised by Soxhlet extraction method and plotting the Insoluble content against the curing time at 150°C. Fig.5 shows that the insoluble content in the cured coating, become almost constant at 96-97% after 3 hours curing at 150°C. Thermal Analysis by TGA of the cured EPD-ENC coating shows (Fig.6) thermal stability of the coating upto 175°C.

Referring to the data plotted in Fig.1 pertaining to increase in thickness against increase in deposition time, it may be noticed that the thickness build-up of EPD coating is almost linear with respect to deposition time at a particular voltage. A defect free and uniform coating on cathode is obtained at a low voltage preferably at less than 30V dc. Higher voltages caused gassing on the electrodes leading to defects and unevenness. Fig.2 above shows that the thickness build-up decreases as the inter-electrode distance is increased.
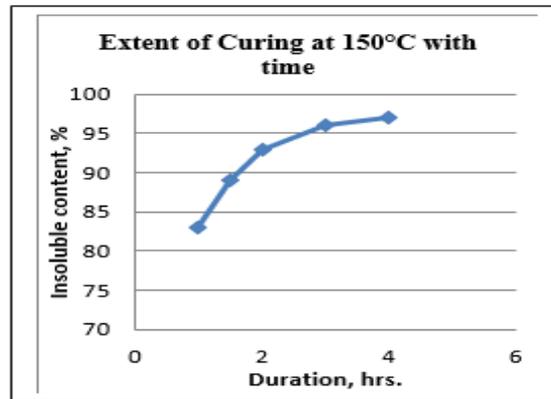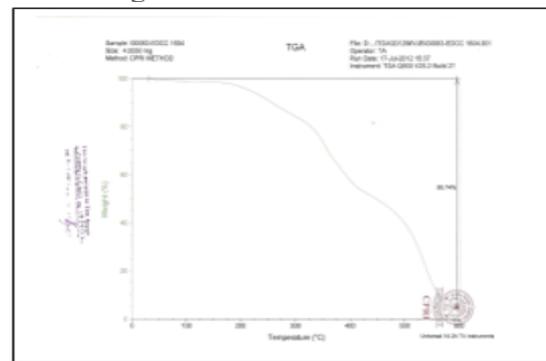

Fig.5: Extent of cure with time

Fig.6: TGA Therrmogram of EPD-ENC

From the Table 3.4 it is observed that there is a increase in the adhesion strength from neat Epoxy coating to Epoxy nano composite containing 4% MMT. Also there is increase in Tensile strength of neat Epoxy coating and Epoxy nano composite coating

5 Conclusions:

i) Modification of DGEBA Epoxy resin has been successfully carried out into a water dispersible and electrodepositable cationic resin.

ii) A novel process for electrophoretic deposition (EPD) of epoxy nanocomposite (ENC) containing a montmorillonite nanoclay has been established and process parameters are established.

iii) Thickness of EPD-ENC coating increases linearly with deposition time.

iv) Thickness of EPD-ENC coating decreases linearly with inter-electrode spacing.

v) Optimum curing of EPD-ENC coatings is achieved at 150°C-3 hours.

vi) Thermal stability of the ENC coating is up to 175°C according to TGA.

vii) Adhesion strength and tensile strength increases from pure Epoxy to Epoxy nano composite containing 4%MMT

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