A Novel Electro-Cathodic Deposition Process For Development Of Polymer Nano-Composites For Electrical And Electronic Application – An Advaced Process For Future

A. K. Shukla[1*], R.M.V.G.K.Rao[2]
[1]Professor of Chemistry, East Point College of Engineering & Technology,Bidarahalli, Bangalore-56OO49, India
[2]Adjunct Professor, Amrita Vishwavidyapeetham University, Coimbatore; Formerly Founder & Head (Retd.),
FRP Division, CSIR-NAL, Bangalore-560017, India
* Corresponding Author's E-mail: ashokshukla52@gmail.com

Abstract:

Polymer Nano-composites (PNCs), by virtue of their functional applications in Engineering and Industry, have been the subject of intense research [1-3] for more than a decade with focus on enhancing their physico-mechanical, thermal and electrical properties. However, currently these Nanocomposites are prepared using the conventional methodology that involves mechanical shear mixing and ultrasonication of nano- particulate fillers into the liquid polymer matrix which poses the limitation of filler loading levels due to resultant viscosity build-up. This limitation remains a serious bottleneck in the present-day conventional technology of obtaining PNCs.

In this article, the authors have presented the development of a novel and eco-friendly process of Electro- Cathodic Deposition (ECD) of an electro-activated polymer matrix, typically a polyepoxide, together with nano-particulates oflayered-silicate nanoclays such as Montmorillonite (MMT), on to a metallic substrate for synthesis of a new class of Electrodeposited Polymer Nano-Composites (EPNC). Such EPNCs are shown [4, 5] to have far superior functional properties as compared to their conventionally prepared counterparts, and are suitable for function specific applications such as dielectrics, anti-corrosion coatings and electrical insulation, intended for electrical, and electronics engineering industry. The advantages of this novel technique are many folds like inherent short processing times, simplicity, and more importantly, obtaining uniformly thick/thin coatings of controlled composition on the substrates, metallic or a composite, of any shape or geometry.

The authors present some highlight of the initial results obtained using this ECD process based on electro- activated epoxy polymer and a layered silicate nanoclay (Montmorillonite) as a composite system on conventional metallic substrate. The results showed significant improvement in dielectric strength and volume resistivity (2 fold and 10 fold respectively) even at low levels of the nanoclay loading (8% by weight of the host polymer), or conversely, facilitates optimally higher filler loadings for super performance functionality requirements without getting into viscosity issues. Another very salient feature of this ECD process is that it is economical and at the same time eco-friendly due to the use of aqueous medium, making it clean and green.

This process is versatile and can be extended to any type of Polymer matrix including the inherently conductive polymers [6, 7] and a semi-conducting nano-filler such as CNTs [8], after suitable functionalisation into their electro-active form required for ECD process. Further studies are in progress to

extend this ECD process to develop EPNC coatings with semiconducting properties using CNTs, dispersed in the same host polymer matrix, targeted for application in EMI shielding of electronic devices including the strategic aircraft systems.

Keywords: Electrocathodic ; Nano-composite ; Electrodeposition ; 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) [9, 10], have led to a paradigm shift in polymer composites technology. Such PNCs are synthesised from the nano-dispersions in polymer matrix which 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, 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 [11] 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 [12-14] 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 and several other commercial applications.

In this article the authors report a novel electro-cathodic 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 nano-composite coatings after cure for their physical, mechanical, electrical and anti-corrosion properties.

Further to above, authors have also projected the versatility of the ECD process to prepare the nanocomposites involving functionalised nano-fillers like carbon nanotubes (CNT), graphene etc. dispersed in the emulsion of epoxy or other polymers including the inherently conducting polymers (ICP) in aqueous medium, and may result in functional PNCs.

2. Experimental

2.1 Materials:

Commercial grade of Epoxy resin based on diglycidyl ether of bisphenol-A (DGEBA) with epoxy value in the range 1.0-1.2 eq./kg without further purification was used to prepare emulsion. Other reagents such as aliphatic amines namely mono-alkyl and dialkyl amines and organic solvents like Ethylene glycol mono butyl ether, Methanol and Xylene and surfactant Triton X-100 of L.R. grade procured from S.D. Fine Chemicals and Thomas Baker India were used in the preparations.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 sizes 100 x 25 mm and 100 x 50 mm with edges rounded off, were used for cathode and anode during EPD process.

2.2 Methods used:

Electro-activation of the epoxy polymer was done by amination of the polymer and the progress 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 Electroactivation of Epoxy Polymer and bath preparation:

Electroactivation of epoxy polymer is carried out by amination process that involves its treatment with amines in the presence of polar solvents like methanol, butyl cellosolve and xylene under controlled heating at temperature (60-70°C) and low-speed (40- 60 rpm) mechanical stirring for 2 to 4 hrs. The extent of the reaction is monitored by measurement of the epoxy equivalent weight of the adduct formed. The product is neutralised with acid to obtain the quaternary ammonium salt which is ionisable in aqueous medium and forms electroactive epoxy emulsion. Nanoclay MMT particulates are dispersed in the emulsion with continuous stirring for several hours followed by ultrasonication at 20 kHz intermittently to ensure thorough dispersion. 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. Nanoclay content can be easily raised up to 10% or more by weight of the polymer without appreciable increase in the viscosity of the formulation.

2.4 Electrophoretic deposition of Nanocomposite:

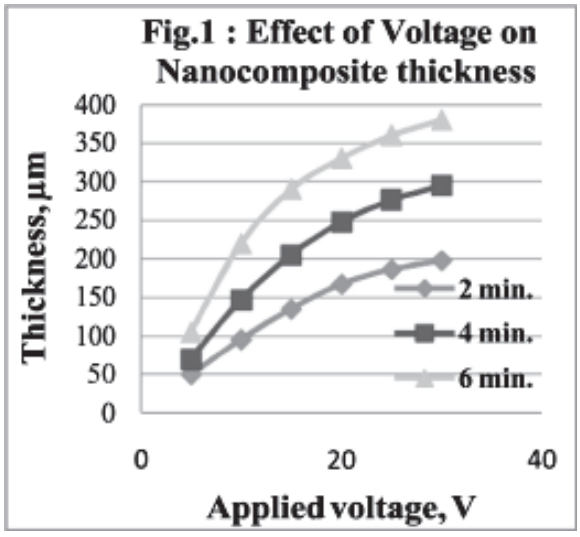
A lab-scale Electrophoretic Deposition (EPD) Cell was fabricated in-house comprising of a plastic container to contain the aqueous electroactive bath formulation prepared as above, equipped with two SS or Al plates acting as cathode and anode, a DC power supply and a magnetic stirrer to stir continuously and slowly the contents of the bath.

On application of suitable DC voltage to the electrodes, the electroactive polycations together with the nanoclay particles discharge and codeposit 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 Effect of Process Parameters on the EPD coating quality:

The process parameters, viz. voltage, time, electrode spacing, bath composition, resin and nanofiller content, that influence the quality of the electrodeposited coating have been studied and summarised below:

(i) Applied Voltage: It directly affects the deposition yield and the thickness. EPD was carried out for the duration of 2, 4, and 6 minutes at different voltages i.e. starting in steps from 5V to 30V.PNC coating specimens were electrodeposited on SS plates, their thickness was measured and the average value was reported. Increase in thickness with applied voltage is shown in Fig.1.



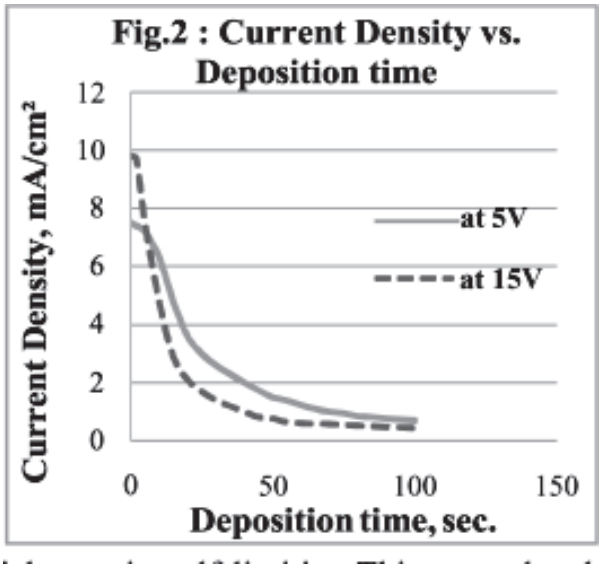
(ii) Current Density: Current density during the EPD process was measured at each voltage applied and was monitored during the entire deposition period. Fig.2 shows the drop in the current density with time at a given applied voltage.

(iii) Breakdown voltage (BDV): It is the rupture or puncture voltage of the cured PNC 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 as shown in fig.3.

(iv) Electrical volume resistivity and corrosion resistance: This characteristic of the electrodeposited PNC coating shows the electrical insulation strength of the coating and has been measured after the curing of the PNC. Retention of Electrical resistivity is used as the measure of corrosion resistance of PNC coating when exposed to corrosive environment such as 4% Salt-fog test for durations of several days as depicted in Fig.4.

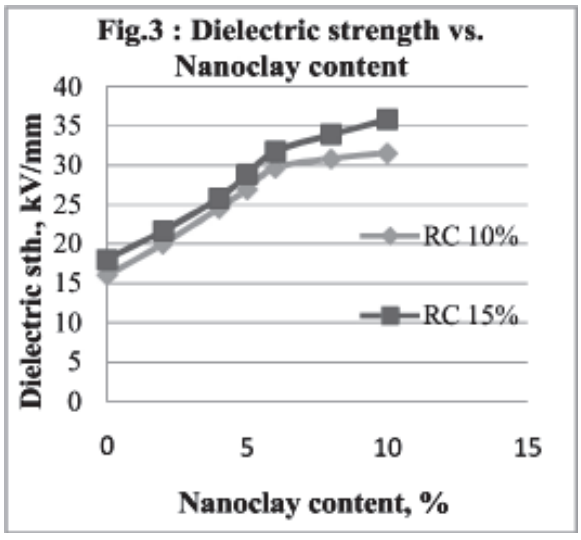
2.6 Characterisation:

The extent of conversion of epoxy resin into adduct during amination process is determined by estimation of epoxy equivalent volumetrically using bromination method as per the international standard ISO 3001-1997(E). The epoxy equivalent weight rises by 2 – 3 times the original value of the base resin indicating the progress of reaction with the formation of adduct having a tertiary amino group in the DGEBA polymer chain. This is confirmed by FTIR spectroscopy by the presence of tertiary nitrogen as sharp bands at 1361 and 1379 cm^{-1} band and the sharp reduction in the intensity of the epoxy group present at 914 cm^{-1} band in the base epoxy resin structure [4]. The nanostructure of the PNC coating is confirmed by XRD and SEM analysis and has been discussed in our earlier article [5]. Dielectric characterisation of EPD-PNCs is carried out by measuring the AC breakdown voltage (BDV), dielectric strength and the volume resistivity of the PNC coatings showing the insulation behaviour of this nanocomposite coating (Fig.3).



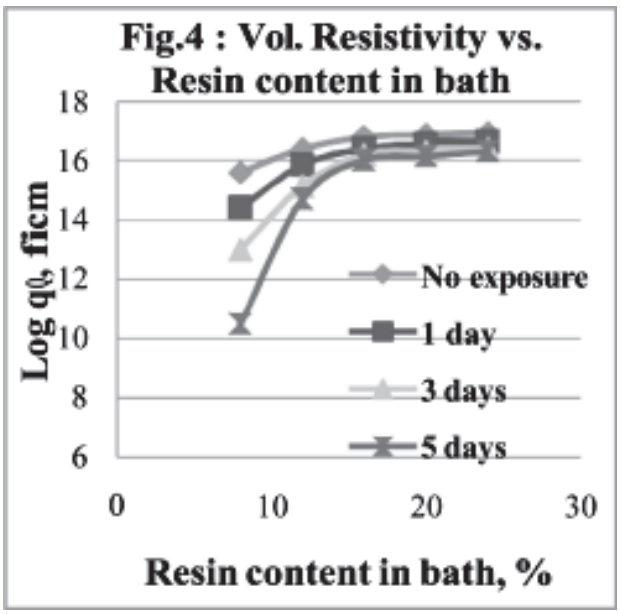
3. Results and Discussion:

The data plotted in the fig.1 shows the positive influence of applied voltage on the thickness build-up of the deposited PNC 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.This can also be explained by the plots in figure 2 that show the drop in current density soon after the start of the EPD process reaching a low value and becomes almost constant after about 90seconds.The drop in current density is steeper at higher applied voltages, in present case at 15 V compared to that at 5 V, as a consequence of faster deposition of PNC at higher voltage leading to higher resistance.



Electrodeposition of PNC 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 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 8- 10 % by weight of the polymer matrix as depicted in the Fig.4. It indicates great scope for insulation application in HV machines.

Corrosion resistance, a significant property of the PNCs has been studied with respect to resin content of the deposition bath by measuring the electrical volume resistivity (considered as indicative of chemical resistance and structural integrity of the PNC coating) of the cured PNCs after prolonged exposure to the salt fog spray (at 4% salt concentration) for 1, 3 and 5 days duration. A plot of logarithm of electrical resistivity (Log q_Q, ficm) under above conditions versus resin content as depicted in Fig.4 clearly shows poor corrosion resistance in PNCs containing 8% nanoclay (by weight of the resin) deposited at lower resin content below 12%, while the PNCs derived from higher resin content bath, show the retention of high volume resistivity or corrosion resistance.



4. Future Scope:

The ECD process for Polymer nanocomposites that involves electroactivation of the organic hydrophobic polymer rendering it water-dispersible or hydrophilic, has the specific advantage of preparing water-based formulations, has great scope of extension to PNCs containing the functionallised nano-fillers such as carbon nanotubes (CNT), single-walled (SWCNT) and multiple walled (MWCNT) types, and ferrites**.** Such PNCs are currently made by conventional methods [12] for EMI shielding application in electronic equipments but to a limited success due to constraints of loading the CNTs resulting in high viscosity build-up. An electroactivated polymer based aqueous formulation and electrodeposition process may hold the key to overcome the above constraints in the technology of PNCs.

5. Conclusion:

Commercial epoxy resin DGEBA type was successfully modified into a water dispersible electroactive cationic polymer. A novel process for electrocathodic deposition (ECD) of epoxy nanocomposite containing a montmorillonite nanoclay has been established. Dielectric strength of neat epoxy ECD coating at 18kV/mm rises to about 35kV/mm at 8% MMT content. Similarly, Volume resistivity of ECD neat epoxy at 4 x 10^{15} ficm rises to 43 x 10^{15} ficm at 8% MMT content, indicating its suitability for electrical insulation application. PNCs show excellent corrosion resistance. The ECD 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 any new class of electrodeposited Polymer nano-composites (EPNCs) on a variety of substrates including FRPs suitable for industrial, electronics and aerospace applications.

6. Acknowledgements:

We acknowledge thankfully the research grant received from DRDO-EMR, New Delhi for initial part of the project. We also thank the EPCET Management for permission to present this work at the ICONEST-2017.

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