

Large scale Eco-friendly Synthesis of Nanoparticulate Fillers for Corrosion Resistant Vinyl Coatings

S.Radhakrishnan*¹ and N.Sonawane
Polymer and Petrochemicals Engineering
Maharashtra Institute of Technology
S124 Paud Road, Kothrud
Pune 411038 India

¹E-mail: radhakrishnan.s@mitpune.edu.in

ABSTRACT

The synthesis of nano particulate CaCO_3 , Fe_2O_3 and BaSO_4 was carried out by green route using the Polymer Mediated Growth (PMG) technique. Large quantities of these nano particles up to few kilograms can be synthesized easily using the PMG method. This is also eco-friendly and green route since it is low temperature aqueous method, does not use toxic chemicals or consume high energy/ electrical power. The particles were characterized by XRD, SEM and TEM to confirm their structure and particle size at nano-levels. These were incorporated at 3-5 wt % in vinyl coatings using polyvinyl acetate or polyvinyl butyral which were coated on mild steel substrates. The corrosion protection was studied using electrochemical impedance spectroscopy (EIS) and monitoring the impedance, open circuit potential, phase etc. over prolonged periods of 150 to 450 hrs at 45 C in saline conditions (3.5% NaCl solution) The nano-particle additives are seen to be 7 to 10 times superior to the commercial grades in corrosion protection. The corrosion protection efficiency of these nano-particle additives is seen to follow the order nano- $\text{CaCO}_3 >$ nano- $\text{Fe}_2\text{O}_3 >$ nano- BaSO_4 in vinyl coatings.

Keywords: nanoparticle fillers, corrosion protection, vinyl coatings

1 INTRODUCTION

Nanocomposites exhibit unique properties distinct from their macro counterparts due to the greater interfacial interactions between the polymer matrix and the additive as a result of increased surface area [1-3]. Lower costs, convenient processing and improved properties are essential for their applications in wide ranging areas. Mineral fillers are traditionally being used in the coatings industry for cost reduction and some property enhancements. The addition of nanoscale fillers can significantly enhance the mechanical, barrier and fire retardant properties[4]. Although the property enhancement and other aspects of nano-materials for plastics are attractive, these are not finding extensive use due to the cost

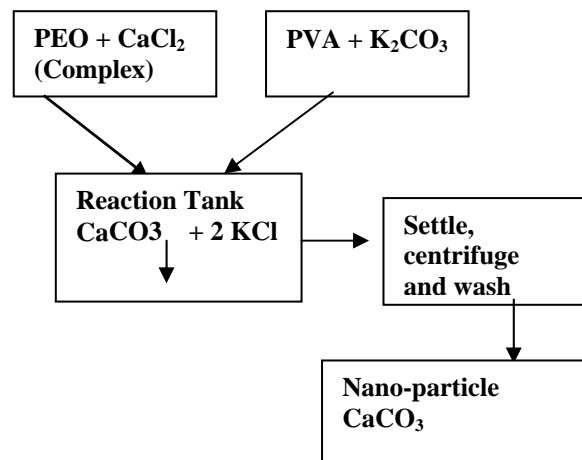
of production and difficulties in handling of the nano-fillers. Polymer mediated growth techniques which has been studied extensively by us, gives a new route to produce the nano-materials on large scale in a cost effective manner. Different types of materials such calcium carbonate, calcium phosphate, iron oxide, zinc oxide, magnesium hydroxide, aluminum tri-hydrate, barium carbonate etc. have been synthesized by PMG technique. We have demonstrated the large scale synthesis of nano-fillers which can be used for anti-corrosion coatings.

2 EXPERIMENTAL

The experimental procedure is described in the following.

2.1 Synthesis of Nanoparticle additives

Polymer mediated growth (PMG) technique [5,6] was used for synthesis of nanoparticles on large scale levels. Typically, the PMG consists of first complexing one of the reactive salts with polyethylene glycol (PEG, polyethylene oxide (PEO) of other ionic polymer. The second reactant is slowly poured on the complex and the ions allowed to diffuse so that the nanoparticles are formed inside the polymer matrix. These are separated by centrifugation, washing etc. The schematics of the PMG process are given in Figure 1.



A few kilos of nanoparticle additives such as CaCO_3 , Fe_2O_3 , BaSO_4 , etc. were prepared following above method using appropriate reactive salts.

2.2 Characterization of Nano-additives

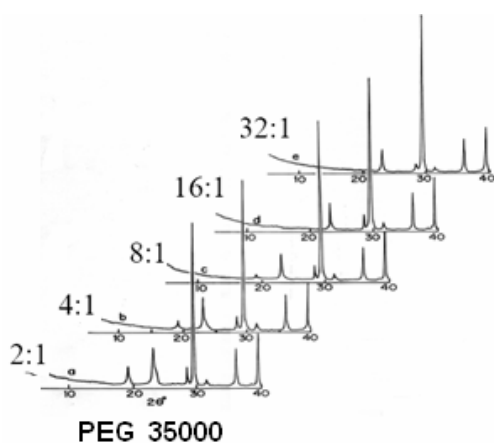
The particles obtained were characterized for their crystal structure, particle size, phase morphology by XRD, SEM and TEM using standard methodology [7].

2.3 Coating formation & Corrosion testing

Polyvinyl acetate and polyvinyl butyral were used as the main matrix. These were dissolved in methanol to form clear stock solution. To this were added the nanoparticulate fillers in different proportions ranging from 1% to 15% and kept in ultrasonicator for 60 min. This assured uniform dispersion of the nanoparticles in the solution. Mild steel substrates which were cut to 50mmx 10 mm rounded edges and polished with fine C-800 emery, washed, cleaned with acetone and dried. These were then dip-coated using the above made dispersions. The coated substrates were allowed to dry at room temperature for 4 hrs and then dried in an oven at 50° C for 4 hrs. For corrosion testing, the coated substrates were placed in 3.5% NaCl solution and periodically removed and examined by Electrochemical Impedance Spectroscopy (EIS) in three electrode cell (working, SCE and Pt counter electrodes) [8,9] The data was obtained in the form of Tafel, Bode and impedance plots. The experiments were carried out for several days.

3 RESULTS & DISCUSSION

Large quantities of nanopowders could be obtained by PMG technique. These were characterized by different techniques to confirm their composition, crystal structure, particle size etc. Figure 2 shows the XRD scans of CaCO_3 obtained with different ratios of PEG (MW35000).



The crystallite size estimated from these data using Scherrer equation are shown in Table-1. It is seen that both molecular weight (MW) and the ratio of the reactant to polymer plays important role on controlling the particle size.

PMG	Calculated crystallite size (nm) with different reactant ratio				
	1:32	1:16	1:8	1:4	1:2
PEG MW					
6000	45	56	72	72	80
20000	18	27	45	51	60
35000	16	25	28.8	36	45

Table 1: CaCO_3 Particle size with respect to MW and reactant ratio in PMG.

Similar studies were carried out for Fe_2O_3 and BaSO_4 . All the data has not been included here due to limited length of the paper. Typical result for Fe_2O_3 are shown in Figures 3 and 4. The comparison of the XRD scans indicates the wide line broadening and nanoparticle formation. The TEM and electron Diffraction confirm the gamma form of Fe_2O_3 [8]. These clearly bring out the fact that PMG can be effectively used for synthesis of nanoparticles of different variety of additives without compromise on the crystalline structure/ phase and stability of material.

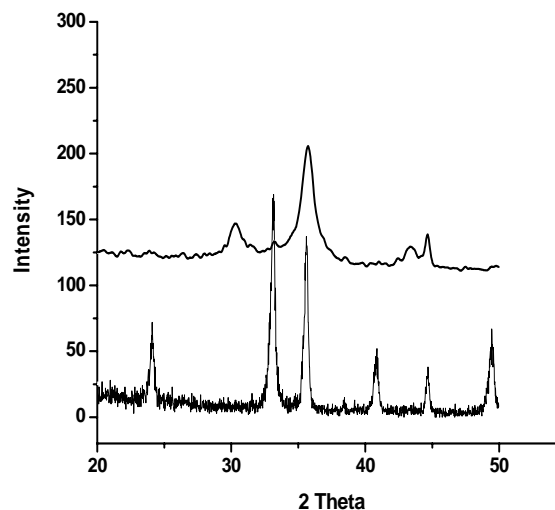


Figure 3: XRD of Fe_2O_3 , top curve from PMG technique Bottom curve is commercial grade.

The stability of the material obtained from PMG technique is mainly because the nanoparticles remain surrounded by a very thin film of the polymer used during synthesis. This thin layer is seen in the TEM of these nanoparticles.

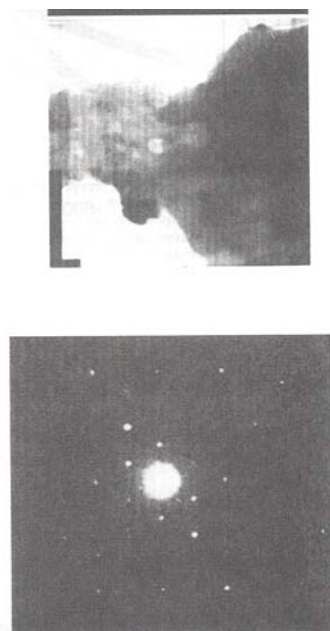


Figure 4: TEM and SEAD of the nano Fe₂O₃ obtained from PMG route.

The results of the corrosion resistance studies of the coatings made from the nanofillers is depicted here in the form of Tafel and impedance plots. Figure 5 shows the

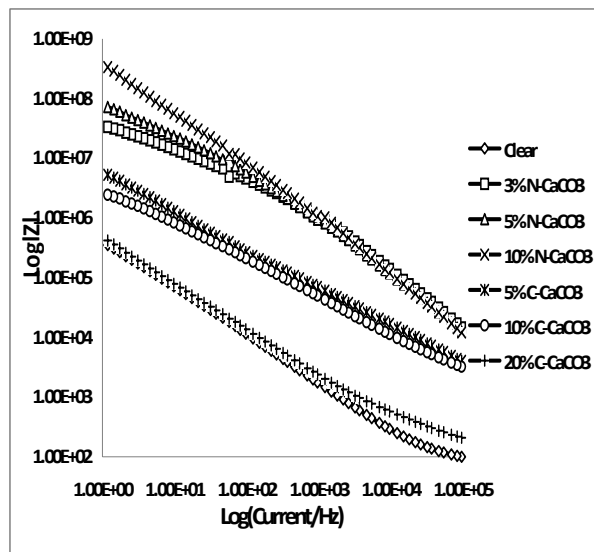


Figure 5: Impedance log $|Z|$ for different composition nano (N) and commercial (C) PVAc - CaCO₃ coatings after 135 hrs at 45 °C in 3.5% NaCl solution.

Impedance after final exposure of CaCO₃-PVAc coatings. Figure 6 shows the Tafel plots of these coatings.

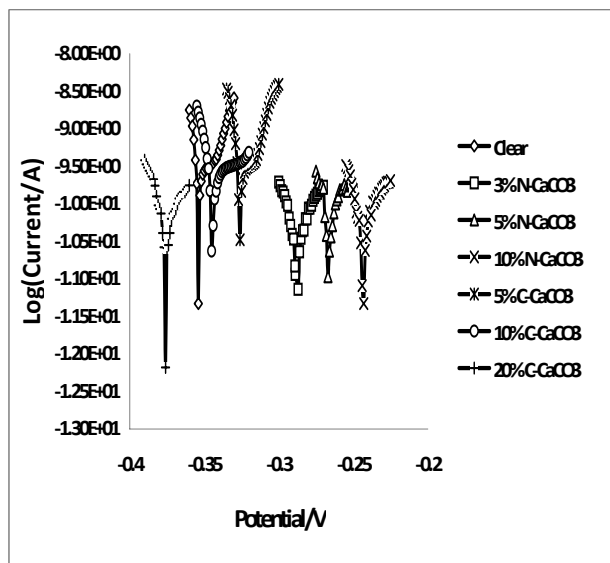


Figure 6: Potentiodynamic polarization curves (Tafel plots) for CaCO₃-PVAc. N:nano, C: macro commercial powder

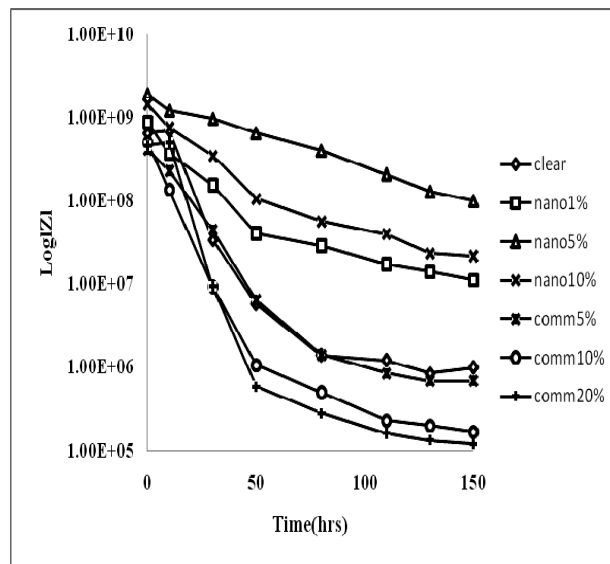


Figure 7: Decay of coating resistance with immersion time for CaCO₃ - PVAc with (N) nano and (C) macro commercial filler

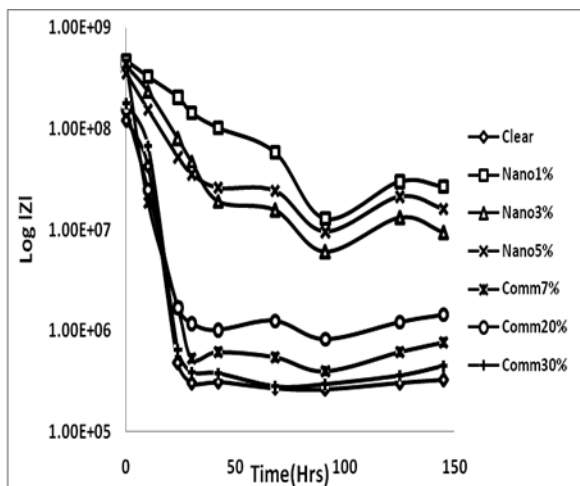


Figure 8 : Decay of coating resistance with immersion Time for Fe₂O₃- PVAc containing (N) nano (C) macro commercial powder

Figures 7 and 8 indicate the decay of coating resistance with time of immersion in the corrosive salt solution (3.5% NaCl at 45 C). The nanoparticle containing coating remain intact even after 150 hours while there is rapid degradation in the coatings with commercial macro particle size fillers.

In order to quantify the relative corrosion protection efficiency, the data was analyzed for all the fillers at following loading levels: for nanosize the range of 3-5% and for macro commercial fillers it was 10%. The decay rate of the coating resistance ($\log |Z|$) was compared with that for blank without any additive taken as the base value. All the data is compiled in Table 2. It is evident that the nano-particle - polymer coatings have much lower decay rate almost $1/10^{\text{th}}$ of the blank or even the commercial fillers. Thus, the nano fillers are all at least 7 to 8 times superior to conventional ones. Further, if one compares the additives within themselves, it is seen that the corrosion prevention efficiency follows the trend $\text{CaCO}_3 > \text{Fe}_2\text{O}_3 > \text{BaSO}_4$

4 SUMMARY & CONCLUSION

The synthesis of nanoparticles on a large scale has been demonstrated by using PMG technique. The main advantage of this process is its easy methodology, use of eco-friendly chemicals, cost effectiveness both due to simple hardware and low temperature processing. The nanoparticles were fully characterized for their structure, particle size and these have been confirmed as regards the expected compounds. The corrosion protection using these

various nano fillers in vinyl coatings has been found to be much superior to the conventional fillers/ additives.

Normalized Log Coat Resist decay/ day			
Additive / Sample	0	3-5% Nano	10% Macro
CaCO ₃ - PVAc	1	0.11	0.77
CaCO ₃ - PVB	1	0.13	1
Fe ₂ O ₃ - PVAc	1	0.28	0.8
Fe ₂ O ₃ - PVB	1	0.35	0.77
BaSO ₄ - PVB	1	0.27	0.95

Table 2: Comparison of corrosion protection by different Nanofiller – polymer coatings

5 ACKNOWLEDGEMENTS

The authors wish to thank Prof.V.D.Karad, Founder president of MAEER, Maharashtra Institute of Technology, Pune together with the Director, National Chemical for their support for completion of this project. They also wish to acknowledge the partial travel grant given by Prof.Karad, MAEER, Pune India for participation at Nanotech 2013.

REFERENCES

- [1] E.P.Gianellis, Adv. Mater. 8, 29, 1996
- [2] R. Dagani, C. & E News. 77, 25, 1999.
- [3] P. C. LeBaron, Z. Wang, and T. J. Pinnavaia, Appl. Clay Sci. 15, 11, 1999
- [4] A. M. Thayer, C. & E News . 81, 15, 2003
- [5] C.Saujanya and S.Radhakrishnan , Polymer, 42, 2255, 2001
- [6] P. Sonawane, S.S Biradar , S. Radhakrishnan, B.D.Kulkami, Mater. Chem. Phys. 105, 348, 2007
- [7] R. Patil, S. Radhakrishnan, Prog. Org. Coat. 57, 332, 2006
- [8] S. Radhakrishnan, C.R. Siju, D.Mahanta, Satish Patil , Giridhar Madras ,Electrochim.Acta, 54, 1249, 2009
- [9] S. Radhakrishnan, N.Sonawane, C.R. Siju, Progr. Org.Coat. (2009) 64, 383