

# Studies on Mechanical and Chemical Characteristics of DGEBA Epoxy/Nano CaCO<sub>3</sub> Nanocomposite Films for Surface Coating Applications

Manoj Kumar Shukla<sup>1</sup>, Deepak Srivastava<sup>2</sup>Research Scholar, Faculty of Engineering and Technology, Mewar University, Chittorgarh, Rajasthan, India<sup>1</sup>Professor, Dept. of Plastic Technology, H.B. Technological Institute, Kanpur, U.P., India<sup>2</sup>

**ABSTRACT:** Epoxy/CaCO<sub>3</sub> nano composites were prepared by mechanical mixing of DGEBA epoxy resin having epoxide equivalent weight (*EEW*) of 180 g/eq and varying concentrations of nano CaCO<sub>3</sub> ranging between 1-10 wt% followed by sonication for 30 min. The prepared Epoxy/nano CaCO<sub>3</sub> mixtures were used for casting films of 100 microns and subjected to curing at 110°C for 1 hr and post curing at 80°C for 5 hrs. The prepared nano composite films were exposed to different acids, alkalies, artificial sea water and solvents for a period up to six months. It was observed that the film containing 5 wt% nano CaCO<sub>3</sub> in epoxy matrix showed maximum resistance to these chemicals. The nano composite films were also tested for various mechanical properties viz. impact resistance, scratch hardness, adhesion & flexibility test. It was found that film containing 5 wt% nano CaCO<sub>3</sub> in epoxy matrix showed maximum resistance to impact, scratch hardness, adhesion and flexibility as compared to other composition of nano composite films and neat epoxy matrix.

**KEYWORDS:** Epoxy Matrix, Nano composite film, DGEBA epoxy resin, Coating, Nano CaCO<sub>3</sub>.

## I. INTRODUCTION

Epoxy resins are the most widely and commonly used thermosetting resins for variety of applications due to their excellent properties such as chemical resistance, outstanding adhesive properties, good mechanical properties and thermal stability [1]. Its applications ranges from chemical resistance coatings, adhesives, floorings, laminating circuit boards and electrical/electronics applications [2-3]. The coating applications of epoxy matrix are not only limited to the metal substrate but also extended to wood, furniture, paper and plastics coatings. The curing of epoxy resin can result a three-dimensional network structure whose properties are dependent on the degree of cross-linking. However, because of its highly cross linked structure, the epoxy resin shows brittleness, crack initiation and propagation and lack of toughness after curing [5-6], which restrict to them for wider applications and showed poor chemical resistance and poor coating properties. The inorganic nano fillers such as nano CaCO<sub>3</sub>, TiO<sub>2</sub>, SiO<sub>2</sub> and clay (particle size  $\leq$  100 nm) incorporation in resin matrix is attracted to encounter these shortfalls [7]. Many researchers proved that the incorporation of nano particles could improve not only the toughness but also the mechanical strength as well as the chemical resistivity of nanocomposite coatings [8].

In present study, the nanocomposite films were prepared by mechanical mixing followed by sonication of epoxy resins and nano CaCO<sub>3</sub> and thereafter casting on panels. The effect of nano size of filler on the mechanical properties viz. impact resistance, scratch hardness, adhesion and flexibility and chemical resistance with various acids, alkalies, artificial sea water and solvents were studied.

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## II. EXPERIMENTAL

### Materials

Diglycidyl ether of bisphenol – A (DGEBA) Epoxy, Grade PG-100 (Viscosity 9000-13000cps) of epoxy equivalent weight 180, procured from Parikh Chemicals Ltd, Kanpur, India (trade name Resinova), nano calcium carbonate (particle size 40-80 nm, sp.gr. 2.5-2.6 gm/cm<sup>3</sup>, cubical shape), from Reinste Nano Ventures Pvt. Ltd., Delhi, hardener (PH851) (Parikh Chemical Ltd, Kanpur) and all acids, alkalies and solvents (S.D. Fine Chemicals Ltd, Mumbai) were used as received.

### Preparation of epoxy/CaCO<sub>3</sub> nano composite films

The DGEBA epoxy resins (PG-100) were mixed with varying amount (i.e. 0, 1, 2, 3, 5 and 10 wt %) of nano CaCO<sub>3</sub>. The mechanical mixing was done at high rpm (4000 rpm) for 30 minutes followed by sonication (using probe type sonicator, model no.750F, PCI, Analytics Pvt. Ltd, Mumbai) for further 30 minutes. The stoichiometric amount of hardener (PH 851) were mixed thoroughly in the resin mixtures. The mixtures were applied on glass and mild steel panels through a Bird film applicator (M/s Sheen instruments Ltd, UK) to form 100 micron film on both panels for each composition of mixtures. These coated panels were cured in an air oven for 1 hr at 110 °C and post cured at 80 °C for 5 hrs. The cured film samples prepared by mixing of 0, 1, 2, 3, 5 and 10 wt % of nano CaCO<sub>3</sub> in epoxy resins were designated as EPC-0, EPC-1, EPC-2, EPC-3, EPC-5, EPC-10, .

### Preparation of chemical reagents and panels

The acids and bases are prepared by diluting them with distilled water to make 10% dilution and the artificial sea water was prepared as per IS:1404 for chemical resistance test. Different panels of mild steel of the size 150 x 100 x 1.25 mm and Glass of size 150 x 50 x 1.25 mm were used, as per IS-101:1986, to evaluate the mechanical and chemical properties of epoxy/nano CaCO<sub>3</sub> composite films respectively.

## III. CHARACTERIZATION OF EPOXY/CaCO<sub>3</sub> NANO COMPOSITE FILMS

### Fourier Transform Infrared (FTIR) Spectra

The Fourier transform infrared spectroscopy (FTIR) was performed on BRUKER FTIR, Vertex series model of BUKER Corporation (U. K.), at room temperature. The FT-IR spectra were recorded in range 400-4000 cm<sup>-1</sup> at a resolution of 2cm<sup>-1</sup> with 10 scans. The background spectra were taken in the empty chamber before measurements to eliminate the influence of moisture and carbon dioxide in air.

### Mechanical Properties

#### *Impact resistance of cured films*

The impact resistance of cured epoxy/CaCO<sub>3</sub> nano composite films were evaluated as per IS:101. The apparatus consisted of steel block (500gm) which slides vertically between two guides. The block was allowed to fall under gravity on to the die block with a hole in the centre. The test panel was placed on the die block and impacted by the steel block. The depth of the indentations were varied by inserting washers of known thickness between the indenter & tool block. The failure of coating films were shown by cracking and the loss of adhesion at the deformed portions of the test panels.

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## Scratch hardness of cured films

The scratch hardness of cured epoxy/CaCO<sub>3</sub> nano composite films were evaluated as per IS:101. The test was performed on mandrel (Make: M/s Sheen Instrument Ltd., U.K.). In this test, a hard hemisphere needle of the diameter of 1 mm was allowed to run on the test panel at rate of 30-40 mm/sec. A specific load was placed on the top of the needle and the panel was examined for sign of bare metal.

## Adhesion and flexibility of cured films

The adhesion and flexibility of cured epoxy/CaCO<sub>3</sub> nano composites films were evaluated as per IS:101 standards. The test was performed on "Mandel" (Make: M/s Sheen Instruments Ltd., U.K.). In this test, the panel was passed through a cylindrical bar of different diameters. At specified cylindrical bar, the panel was examined for sign of cracking flapping and detachment from the substrate, after the sample had been bent through 180°C.

## Morphological Properties

The scanning electron microscope (SEM) images were obtained by using high resolution and low vacuum SEM equipment of FEI Company, USA; model no. Quanta 200 FEG to investigate the microstructure and fractured surfaces of nano composites. The samples were mounted on aluminium stubs using carbon tape. The samples were coated with a thin layer of platinum to prevent charging before the observation by SEM.

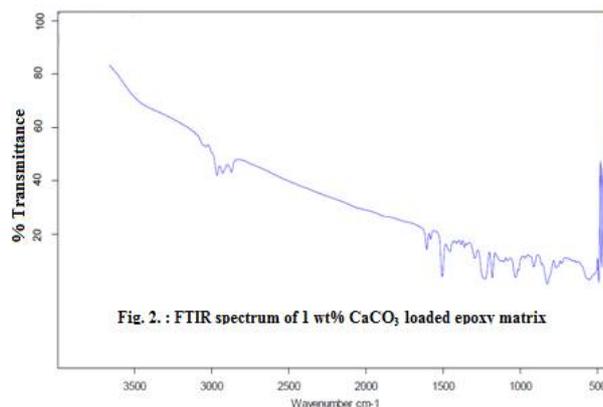
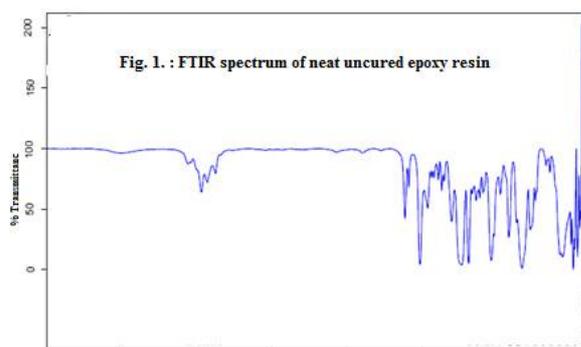
## Chemical Resistance

The glass panels were immersed in different acids, alkalies, artificial sea water and solvents for six months. The observation was noted at every one month interval. The coated glass panels were half dipped in the chemical reagents and rest of the portion was left unexposed to compare the film properties.

## IV. RESULTS AND DISCUSSIONS

### FTIR spectroscopic analysis

The IR spectra of uncured neat epoxy resin and 1 wt% CaCO<sub>3</sub> loaded epoxy resin have been given in Fig.1 and Fig.2, respectively. The absorption band at around 3500 cm<sup>-1</sup> and 913 cm<sup>-1</sup> were due to the -OH and oxirane group stretching in neat epoxy resin matrix, respectively. Similar absorption bands were also appeared in case of 1 wt% CaCO<sub>3</sub> loaded epoxy resin. It revealed the non reactivity of nano CaCO<sub>3</sub> towards the epoxy resin. Hence, it can be concluded that the nano particles were physically blended in the resin system.

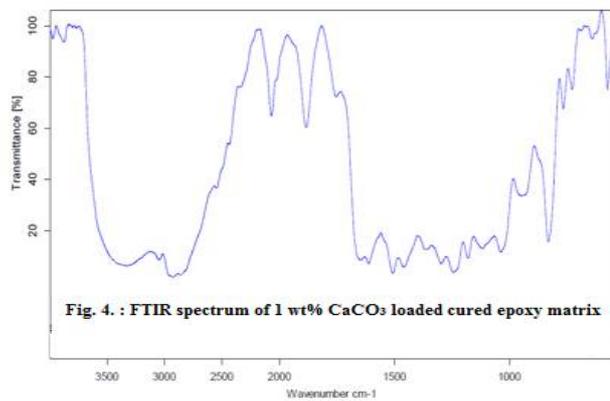
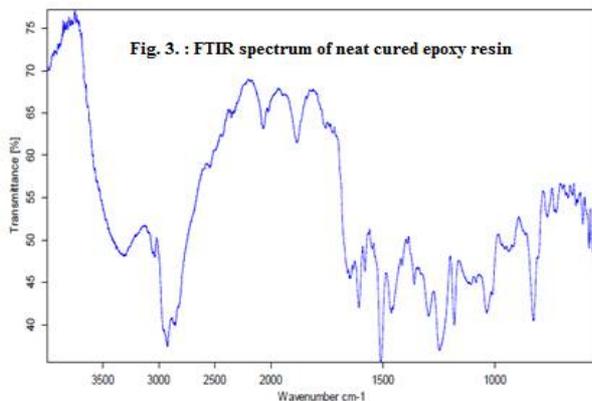


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The IR spectra of neat and 1 wt%  $\text{CaCO}_3$  loaded cured epoxy matrix have been given in Figs.3 and 4, respectively. The hydroxyl group formed due to the reaction of oxirane group of epoxy resin and primary amine which was identified from the appearance of bands near the  $3355\text{ cm}^{-1}$  and  $3500\text{ cm}^{-1}$ . The primary amine convert in to secondary amine and further to tertiary amine during the curing reaction. This conversion led to the evolution of  $-\text{OH}$  groups. A broad absorption peak near  $3300\text{ cm}^{-1}$  showed the increase in the number of  $-\text{OH}$  groups due to reaction between oxirane groups and the amines. The similar bands were appeared for 1 wt%  $\text{CaCO}_3$  loaded cured epoxy matrix. This revealed that nano  $\text{CaCO}_3$  in the epoxy matrix remained unreacted. The oxirane group cleavage was confirmed by the absence of bands around  $913\text{ cm}^{-1}$  of the both the cured matrices.



### Studies on Mechanical Properties of Cured Films

The data related to mechanical properties viz. Impact resistance height, scratch hardness and adhesion and flexibility test with respect to 0, 1, 2, 3, 5, 10 wt% of nano  $\text{CaCO}_3$  of cured films have been given in Table 1.

#### Impact resistance

It has been observed that the impact resistance of nano composite films increased as the nano  $\text{CaCO}_3$  loading increased and found maximum for 5 wt % loading of nano  $\text{CaCO}_3$  in cured resin matrix. Further loading of nano  $\text{CaCO}_3$  in resin matrix led to decrease in impact resistance. It revealed that large quantity of nano filler led to the agglomerate and causes the deterioration of toughness of cured epoxy nanocomposite films. It was observed that nano  $\text{CaCO}_3$  exhibits reinforcing capacities when added in small quantity. We also found that the improvement in the impact resistance might be due to load sharing by the nano particles and the intermolecular force of attraction between macro molecules of resin and nano particles due to hydrogen bonding, which enhanced the toughness of resin matrix at fully cured stage. These results are supported by R. Jain et al. [9]

#### Scratch hardness

It has been observed that the scratch resistance of nano composite films increased as nano  $\text{CaCO}_3$  loading increased and found maximum for 5 wt % loading of nano  $\text{CaCO}_3$  in epoxy matrix and decreased thereafter as the content of nano  $\text{CaCO}_3$  increased. This might be due to nano particles aggregations which causes reduction in toughness and poor bonding between matrix and nano particles in nanocomposite films. Hence, it can be concluded that the improvement in the scratch hardness was found maximum in 5 wt%  $\text{CaCO}_3$  loaded nano composite films due to the surface hardening by nano particles. These result are supported by C.B. Ng et al. [10]

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## Adhesion and flexibility test

All the cured film samples showed poor flexibility except 5 wt% CaCO<sub>3</sub> loaded nano composite film. The failed samples may be attributed to higher cross link density & curing at elevated temperature and led to lower toughness. Passed sample showed higher toughness due to uniform distribution of nano CaCO<sub>3</sub> in the resin matrix and the hydrogen bonding between the polymer chains and the nano particles.

	Sample Code	Nano CaCO <sub>3</sub> content (%)	Impact height (cm)	Scratch hardness (kg)	Adhesion & flexibility (Bond test)
1.	EPC-0	0	6	4.2	Fail
2.	EPC-1	1	7	4.3	Fail
3.	EPC-2	2	10	4.5	Fail
4.	EPC-3	3	20	4.8	Fail
5.	EPC-5	5	40	5.2	Pass
6.	EPC-10	10	30	4.8	Fail

**Table 1: Experimental data of impact height, scratch hardness, adhesion and flexibility test of epoxy nano composite film samples.**

## Studies on chemical resistance

The nano composite cured films were remain unaffected for maximum periods when 5 wt% CaCO<sub>3</sub> content was used. The maximum periods for 5 wt% loaded CaCO<sub>3</sub> were 5,3,4,5,4,5,4,5,5,5 and 5 months towards artificial sea water, HCl, H<sub>2</sub>SO<sub>4</sub>, CH<sub>3</sub>COOH, NaOH, NH<sub>4</sub>OH, xylene, CH<sub>3</sub>OH and toluene respectively as compared to neat and other compositions of cured films. It has been shown in the figure 5.

This could be explain, as the content of nano CaCO<sub>3</sub> increased in epoxy matrix it blocks the free spaces between macromolecules in cured nano composite films up to 5 wt%, hence the penetration of these chemicals were remain restricted for maximum duration (5 months) up to 5 wt% CaCO<sub>3</sub> containing film. This results the improvement in chemical resistivity of nanocomposite films and beyond 5 wt%, chemical resistivity decreased due to the aggregation of nano particles. These result are supported by A, Kumar et al. [8]

We also found the unaffected duration of nanocomposite films in case of HCl is less than other chemicals. It showed that the hydroxyl groups present in resin matrix are more reactive towards HCl than other chemical reagents.

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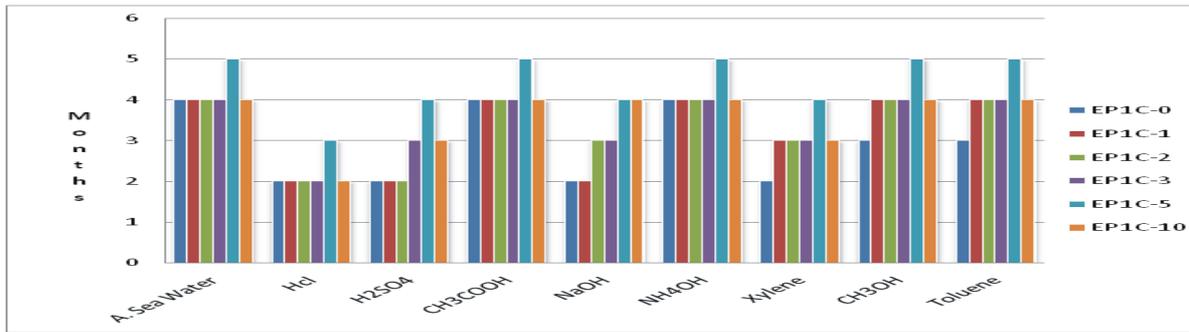


Fig.5 Chemical Resistance of nano composite films

## Morphological Studies

The surface morphology of fractured sample of neat epoxy matrix has been given in the figure 6. The surface of the neat matrix appears smooth. This led to the brittleness and the crack initiation and propagation in the neat epoxy matrix.

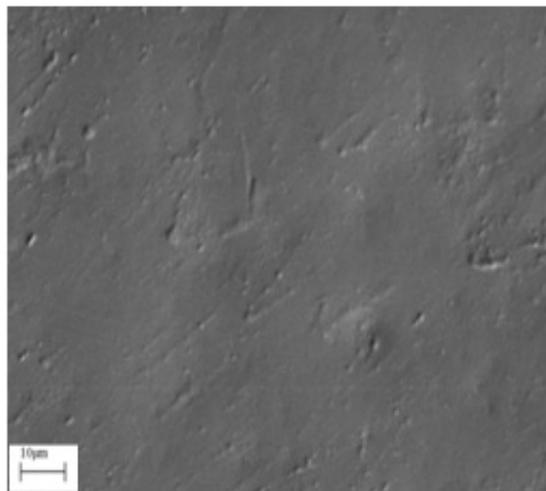


Fig.6 SEM micrograph of neat matrix

The SEM micrograph of 5 wt% CaCO<sub>3</sub> loaded matrix showed the uniform dispersion of nano particles throughout the matrix system as shown in the figure 7, which enhances the mechanical properties of nano composites. It was also observed that the fractured surface became rougher after the nano particle loading. It revealed that the increase in the surface roughness increases the surface area which deflect the crack propagation. The surface roughness also increases the absorbed energy of fracture during the deformation of the cured matrix. The increase in absorbed energy enhances the fractured toughness of nano composite system. This investigation has been supported by H.Alamri et al. [11].

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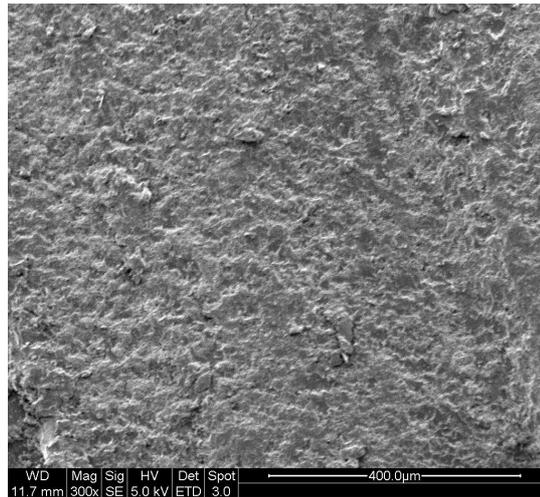


Fig.7 SEM micrograph of 5 wt% CaCO<sub>3</sub> loaded matrix

## V. CONCLUSIONS

From these results, it can be concluded that the dispersion of nano particles in the epoxy matrix had drastic effect on the properties of resultant coating films. The incorporation of nano CaCO<sub>3</sub> in epoxy matrix improves the impact resistance, scratch hardness, adhesion and flexibility and the chemical resistance towards the various chemicals as compared to the neat epoxy matrix. It is also clear from SEM micrograph images the uniform distribution and the fractured surface roughness were increased as the nano CaCO<sub>3</sub> content in the epoxy matrix increased, which absorbed more energy to crack propagation and pinned the crack initiations. The maximum impact resistance, scratch hardness, adhesion and flexibility and chemical resistance were found, when the 5wt% content of nano CaCO<sub>3</sub> was used with respect to other compositions of nano CaCO<sub>3</sub> and neat epoxy matrix.

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