

DGEBA Epoxy Nano Composite: A Study on Mechanical Properties Characterization

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Abstract: Epoxy/CaCO₃ 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 CaCO₃ ranging between 1-10 wt% followed by sonication for 30 min. The prepared Epoxy/nano CaCO₃ mixtures were poured into the Teflon mold and subjected to curing at 110°C for 1 hr and post curing at 80°C for 5 hrs. The prepared nano composite samples were investigated for mechanical properties viz., tensile strength, elongation-at-break and elastic modulus, impact strength and Shore D hardness. It was observed that the sample containing 5 wt% nano CaCO₃ in epoxy matrix showed maximum tensile strength, elongation-at-break, the impact strength and hardness as compared to other samples and neat epoxy matrix. The samples were also investigated for curing mechanism by FTIR and DSC, for morphology by SEM.

Keywords: Epoxy matrix, nano composites, DGEBA epoxy resin, nano CaCO₃, hardener.

1. Introduction

Epoxy resins are versatile and most commonly used thermosetting resins for number of applications such as coatings, floorings, adhesives, non conducting materials, encapsulations and electrical/electronics applications, due to their excellent mechanical properties [1-2]. But, it becomes brittle when cured that restricts to number of applications due to poor mechanical properties [3-4]. The studies showed that the incorporation of nano size fillers in the epoxy resin can drastically improve the mechanical properties [5-6]. The reinforcement of epoxy matrix by the inorganic fillers such as TiO₂, ZnO, nano clay, carbon nano tubes and CaCO₃ were attracted to many researchers and scientists. The addition of nano fillers (particle size < 100 nm) in the epoxy matrix affects greatly to the properties of nano composites due to their larger surface area and the homogeneous dispersion within the macro molecules up to certain extent [7-8]. However, one basic problem associated with the nano fillers is the tendency to agglomerate during the mixing with the resin matrix [9]. This shortfall can be bridged by prolong mechanical mixing and followed by ultra sonication of the filler/resin mixture [10].

In present study, the nanocomposites were prepared by mechanical mixing followed by sonication of epoxy resins and nano CaCO₃. The effect of nano size of filler on the mechanical properties viz., tensile strength, elongation-at-break, impact strength and hardness was studied.

2. Experimental

2.1 Materials

Diglycidyl ether of bisphenol – A (DGEBA) Epoxy (m/s Parikh Chemicals Ltd, Kanpur, India; Grade PG-100; EEW:180 eq/g; trade name: Resinova; Viscosity: 9000-13000cps, nano calcium carbonate(m/s Reinste Nano Ventures Pvt. Ltd., Delhi; particle size: 40-80 nm; sp.gr.: 2.5-2.6 gm/cm³, cubical shape) and polyamide hardener (m/s

Parikh Chemical Ltd, Kanpur; Grade: PH851 were used as received.

2.2 Preparation of epoxy/CaCO₃ nano composites

The DGEBA epoxy resin was mixed with varying amount of nano CaCO₃. The mechanical mixing was done at high rpm (4000 rpm) for 30minutes followed by sonication (Probe type sonicator; M/s PCI, Analytics Pvt. Ltd, Mumbai; model no.750F) for further 30 minutes. The stoichiometric amount of hardener (polyamide) was mixed thoroughly in the resin mixtures. The mixtures were then poured into a Teflon mold and mold was placed in an air oven for 1 hr at 110°C for curing and post curing at 80°C for 5 hrs. The cured nano composite samples were designated as EPC-0, EPC-1, EPC-2, EPC-3, EPC-5, EPC-10 based on the amount (i.e. 0, 1, 2, 3, 5 and 10 wt %) of nano CaCO₃ in epoxy resin.

3. Characterization of Nano Composites

3.1 Fourier Transform Infrared (FTIR) Spectra

The Fourier transform infrared spectroscopy (FTIR) of cured and uncured epoxy resin matrices (pure and nano CaCO₃ mixed resin matrix) was performed on Bruker FTIR (M/s BUKER Corporation U. K.; Vertex series model) at room temperature. The FTIR spectra were recorded in the range of 400-4000 cm⁻¹ at a resolution of 2 cm⁻¹ 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.

3.2 Mechanical Properties

3.2.1 Determination of Tensile Strength, Elongation-at-break and elastic modulus:

Dumb-bell shaped samples were prepared and were used for the determination of the tensile strength, elongation-at-break and elastic modulus. The samples were prepared in a self designed teflon mould as per ASTM D638 specification.

Both ends of samples were tightened in the metallic grips of Universal Testing Machine (M/s Zwick Roell Pvt Ltd, Germany; model: Z010M) with cross head speed at 25mm min⁻¹. The tensile strength, elongation-at-break and elastic modulus values were automatically recorded on computer screen.

3.2.2 Determination of Impact Strength and Shore D hardness

The test specimens for Izod Impact were prepared according to ASTM D-256. The size of the specimens were 2.5 x 0.5 x (1/8) inch with a recommended notch depth of 0.100 inch. The test specimen was clamped on to the impact testing machine (M/s CEAST[®] Resil Impactor, Germany; Model: 6957) in the position so that notched end of the specimen was facing the striking edge of the pendulum. Now, the pendulum hammer was released, allowed to strike the specimen and swing through. If the specimen did not break, more weights were attached to the hammer and the test was repeated until failure was observed. The impact strength was read directly from the dial attached to the tester. The hardness of prepared nano composite samples was measured by using the shore D hardness tester as per ASTM D 2240. The determination of hardness is based on the force applied on the sample continuously without shock and measured the depth of indentation on the surface of the samples.

3.3 Curing Studies

For curing studies, freshly prepared samples obtained by mixing stoichiometric amount of polyamide hardener and DGEBA epoxy resin were used for recording of DSC traces. The curing process were performed by using DSC Q200 (M/s T A Instruments, USA). The temperature range was taken from 25-300°C with the heating rate 10°Cmin⁻¹ in the nitrogen atmosphere.

3.4 Morphological Properties

The scanning electron microscope (SEM) images of the fractured surface of samples were obtained by using high resolution and low vacuum SEM equipment (M/s FEI Company, USA; model: 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.

4. Results and Discussions

4.1 Infra Red Spectroscopic Studies

The FTIR spectra of samples EPC-0 and EPC-1 have been shown in Figs.1-2, respectively. The absorption band at around 3500 cm⁻¹ and 913 cm⁻¹ were due to the hydroxyl (-OH) and oxirane group stretching of neat epoxy matrix, respectively. Similar absorption bands were also appeared in EPC-1 sample. It revealed the non reactivity of nano CaCO₃ towards the epoxy matrix. Hence, it can be concluded that the nano particles were physically blended in the matrix system.

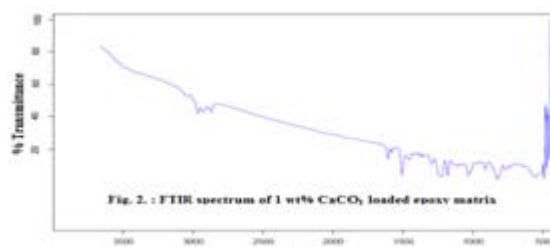


Fig. 2 : FTIR spectrum of 1 wt% CaCO₃ loaded epoxy matrix

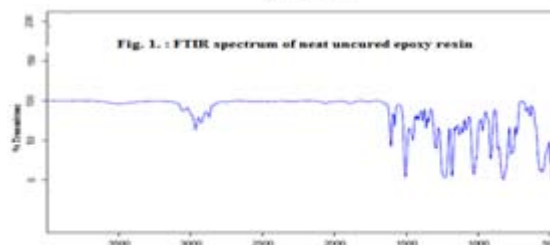


Fig. 1 : FTIR spectrum of neat uncured epoxy resin

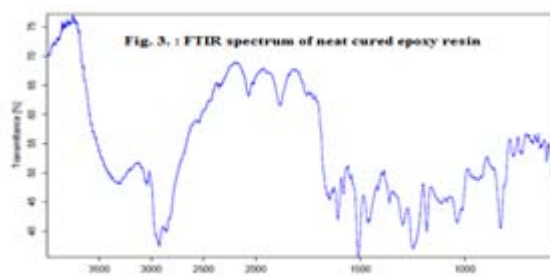


Fig. 3 : FTIR spectrum of neat cured epoxy resin

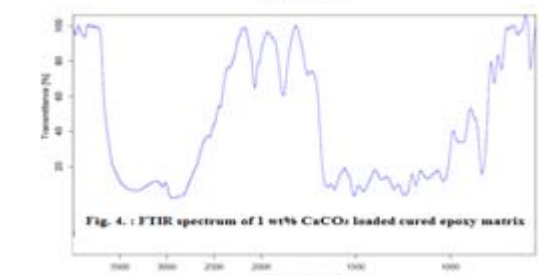


Fig. 4 : FTIR spectrum of 1 wt% CaCO₃ loaded cured epoxy matrix

The IR spectra of neat and 1 wt% CaCO₃ loaded cured epoxy matrix have been shown in Figs. 3-4, respectively. The hydroxyl group formed due to the reaction of oxirane group of epoxy resin and primary amine of hardener, which was identified from the appearance of bands near the 3355 cm⁻¹ and 3500 cm⁻¹ wavenumber. The primary amine convert in to secondary amine and further to tertiary amine during the curing reaction. This conversion led to the evolution of -OH groups. A broad absorption peak near 3300 cm⁻¹ showed the increase in the number of -OH groups due to reaction between oxirane groups and the amines. The similar bands were also appeared for 1 wt% CaCO₃ loaded cured epoxy matrix. This showed that the nano CaCO₃ in the epoxy matrix remained unreacted. The oxirane group cleavage was confirmed by the absence of bands around 913 cm⁻¹ of the both the cured matrix.

Table 1: Data obtained from DSC scans of nano composites

Sample	Nano CaCO ₃ (wt%)	¹ T _i (°C)	² T _o (°C)	³ T _p (°C)	⁴ T _f (°C)	⁵ ΔH (J/g)
EPC-0	0	29.54	55.44	100.65	134.10	68.93
EPC-1	1	29.50	54.63	99.52	122.73	163.00
EPC-2	2	29.55	53.85	99.11	121.81	198.15
EPC-3	3	27.27	54.10	99.04	118.50	199.20
EPC-5	5	22.73	52.65	98.65	112.5	210.70
EPC-10	10	22.50	51.53	97.37	112.27	218.90

- 1 – Kick off temperature, Where curing starts
- 2 - Temperature where first detectable heat is released. It was obtained by extrapolation of the steepest portion of exotherm
- 3– Temperature of peak position of exotherm
- 4 – Temperature of the end curing of the exotherm
- 5 –Heat of curing was calculated by measuring the area under the exothermic transition

4.2 Curing Studies

The DSC scan data of neat epoxy and nano-CaCO₃ loaded resin matrix for T_i, T_o, T_f, T_p and heat of curing ΔH, of all the samples are summarized in table 1. It is evidence from the table that the values of T_i, T_o, T_f, and T_p were decreased as the concentration of nano CaCO₃ increased, while the ΔH value increased as the concentration of nano CaCO₃

increased. It was clear from the results the nano CaCO₃ did not affect the curing reaction of epoxy resin with polyamide [11]. A single peak appeared in DSC scans of all samples, here, DSC scans of only samples EPC-0 and EPC-5 have been shown in figs. 5(a) and 5(b). It is cleared from the scans that the peaks of epoxy resin shifted towards lower temperature with the addition of nano-CaCO₃. This might be possible due to nucleophilic addition to epoxide with primary and secondary amines and the proton donor such as acid acted as catalyst which accelerated the epoxide-amine ring opening reaction and the hydrogen bonds were formed between the oxygen of epoxide and the hydrogen of the stearic acid on the surface of nano calcium carbonate, resulted the acceleration of epoxide-amine curing reaction [12].

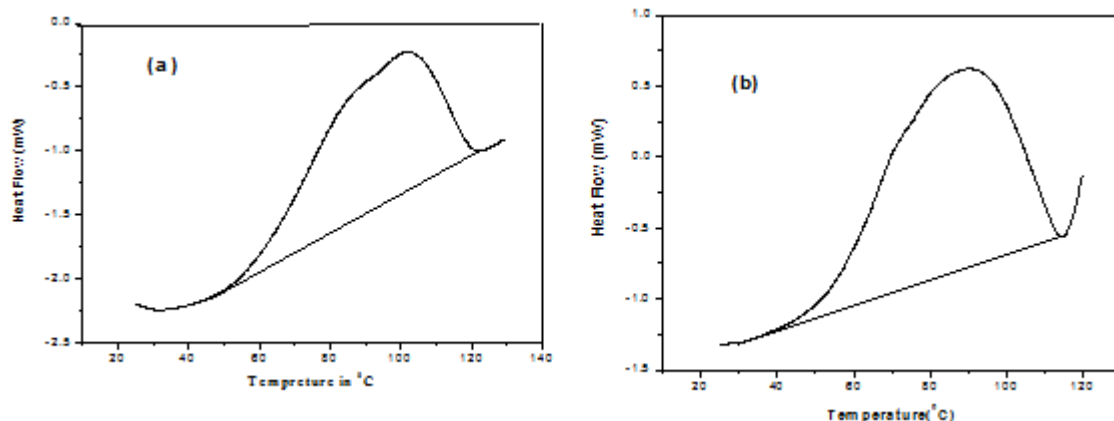


Figure 5: Dynamic DSC Scan of Samples (a) EPC-0 (b) EPC-5

4.3 Studies on Mechanical Properties

4.3.1 Tensile Strength and Elongation-at-Break

The results of tensile strength and elongation-at-break are summarized in the Table 2, it is evidence from the results that the increase in loading of nano-CaCO₃ in epoxy matrix increased both the tensile strength and elongation-at-break. The values of tensile strength and elongation-at-break was found to be maximum in 5 wt% nano-CaCO₃ loaded nano composite sample. The increase of tensile strength and elongation-at-break might be due to the filling of nano particles into the amorphous region of matrix via uniform dispersion up to 5 wt%. When the amorphous region of epoxy matrix had been completely filled by the nano particles, the sample achieved maximum tensile strength due to the load shearing by nano particles. The nano composite samples also showed the toughening behavior on addition of nano filler for same composition, which led to enhance the elongation-at-break values. Beyond 5 wt% addition of nano CaCO₃ in the epoxy matrix led to the agglomerate. This might be resulted the decrease in the tensile strength and the elongation-at-break [13]. Fig.6 showed the variation of tensile strength and elongation-at-break with the increase in the concentration of nano CaCO₃. The tensile strength and elongation-at-break was increased up to 5 wt% addition of nano CaCO₃ and decreased thereafter.

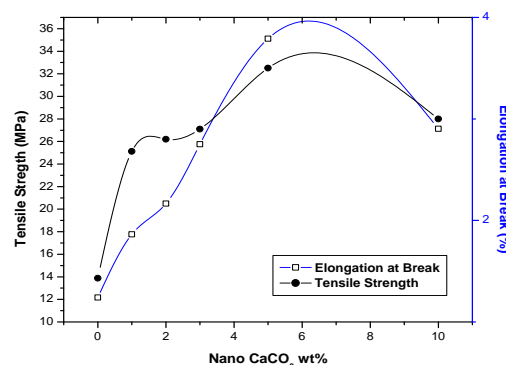


Figure 6: Variation of tensile strength and elongation-at-break with percentage loading of nano-CaCO₃ in epoxy matrix

Table 2 also showed the values of impact strength of all nano composite samples. It is obvious from the table that the increase in the content of nano CaCO₃ in the matrix, increased the impact strength of nano composite samples and found maximum in 5 wt% CaCO₃ loaded nano composite sample. The reason behind such improvement might be due to the higher surface area of nano particles, which exfoliated/intercalated in the epoxy matrix. The higher surface area might also be resulted higher energy of absorption during the load. The further loading of nano CaCO₃ might convert into agglomeration and resulted the weak bonding between the nano filler particles and the macro molecules.

Table 2: Experimental data sheet for mechanical properties of nano composites

S.N.	Sample code	Tensile Strength (Mpa)	E-Modulus (Mpa)	Elongation at Break (%)	Impact Strength (kJ/m ²)	Shore D Hardness
1.	EPC-0	12.17	55.62	1.43	1.20	30
2.	EPC-1	17.77	62.04	2.68	1.40	35
3.	EPC-2	20.50	74.77	2.80	1.75	45
4.	EPC-3	25.75	79.80	2.90	2.20	52
5.	EPC-5	35.12	84.04	3.50	2.90	60
6.	EPC-10	27.13	78.03	3.00	2.40	55

4.3.2 Elastic Modulus of Nano Composites

The variation of elastic modulus with nano-CaCO₃ loading is shown in fig. 7. As the nano CaCO₃ content increased in the epoxy matrix, the elastic modulus also increased and showed the maximum value (84.04 Mpa) at 5 wt% CaCO₃ loaded nano composite sample. This improvement might be due to higher exfoliation of nano filler in the matrix system, which enhances the toughening behavior in the nano composite systems.

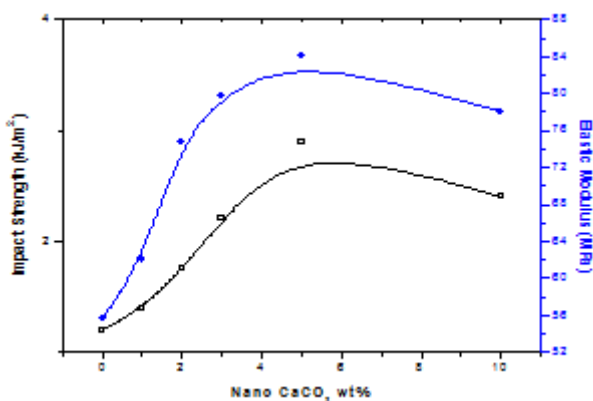


Figure 7: Variation of impact strength and elastic modulus with nano- CaCO₃ loading in epoxy matrix

4.3.3 Shore D Hardness

The effect of nano particulates on the hardness of epoxy nano composites with respect to the varying concentration of nano CaCO₃ have been shown in the fig. 8 and the experimental observation are shown in table 2. By seeing the figure and table it can be easily assessed about the trends of the hardness achieved by nano composite samples. That is, as the nano particles loading increased in the nano composite samples, the hardness shore D value also increased and observed maximum value in the sample EPC-5 with filler loading of 5 wt%. The increment was found from 30 to 60. Hence, the samples with higher concentration of nano particles showed higher resistance to the indentation force therefore exhibiting higher Shore D values. This could be attributed to the inherent hardness of the CaCO₃ particles compared with neat epoxy, which affects the overall hardness of prepared nano composite samples and become more prominent at higher concentration. But as soon as the loading of nano filler increased beyond 5wt% the hardness value decreased. The decrement in the hardness could be

attributed to the floccules of nano filler and developed a perforation in confined region within the nano composites.

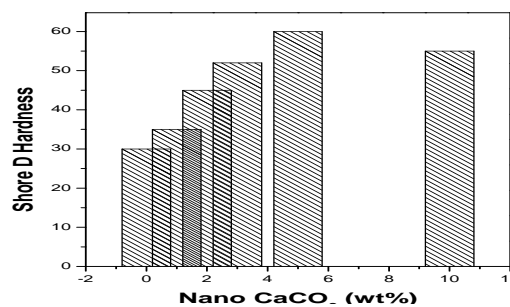
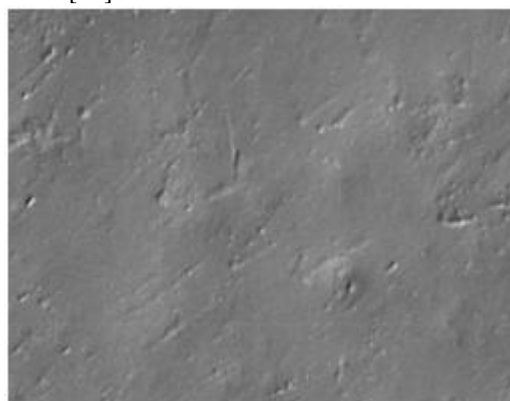


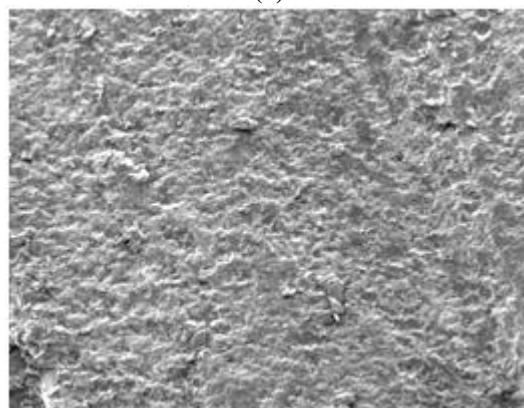
Figure 8: Shore D hardness of nano composites with different concentration of nano CaCO₃

4.3.4 Morphological Studies

The SEM images of fractured surface of neat matrix and 5 wt% loaded matrix have been shown in figs. 11(a) and 11(b). The SEM image of sample EPC-0 showed less surface roughness than as seen in the SEM image of sample EPC-5. The lower surface roughness indicating more possibility of crack initiation and propagation. It is obvious that, as the loading of nano CaCO₃ increased in the epoxy resin matrix the roughness of the fractured surface also increased. The increase in the surface roughness increased the surface area to deflect the crack initiation and propagation and also increased the absorbed energy of fracture by the crack length during the deformation in the samples. The higher energy absorption enhanced the fracture toughness of the nano composite samples. Hence, it could be concluded that the 5wt% of CaCO₃ loaded nano composite sample have better exfoliation of nano particulates within the matrix and maximum surface roughness as compared to the neat epoxy resin matrix [14].



(a)



(b)

Figure 11: SEM image of samples (a) EPC-0 (b) EPC-5

5. Conclusions

The following conclusions can be drawn:-

- 1) As the concentration of nano calcium carbonate increased in the nano composite samples, the tensile strength, elongation-at-break, impact strength, elastic modulus and hardness increased and found maximum in EPC-5 sample and thereafter decreased due to the agglomeration of nano particles in the matrix. The improvement in the mechanical properties of nano composite samples were due to load sharing by nano particles, when subjected under load.
- 2) The high degree of exfoliation/ intercalation of nano particles was observed in EPC-5 sample than other nano composites, which showed the higher roughness and surface area to divert the crack initiation and propagation.
- 3) The curing reaction between the epoxy resin matrix and the polyamide hardener was confirmed by the FTIR spectrum i.e. the absorption band around $3350\text{-}3450\text{ cm}^{-1}$ was broaden during the curing reaction, which indicated the generation of hydroxyl group and cleavage of epoxide ring. The disappearance of absorption band near 913 cm^{-1} confirmed the consumption of oxirane groups during the cross-linking reaction. It was also observed by DSC dynamic thermograms of nano composite samples that, the nano CaCO_3 did not effect the curing reaction in any way.

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