Effect of Nano Filler Reinforcement on Mechanical Properties of Epoxy Composites

Suresha B1 *, C A Varun1, Indushekhara N M1, Vishwanath H R1 , Venkatesh1
1 Department of Mechanical Engineering, The National Institute of Engineering, Mysuru, India

E-mail: sureshab@nie.ac.in

Abstract
Nano-sized functional fillers, such as Nano-clay (N-C) and Nano-calcium carbonate (N-CC), have attracted a great deal of awareness due to their unexpected intrinsic properties. Extensive research has been done on clay material for epoxy Nanocomposites but only a few have ventured into a comparison with other Nanofillers. In this paper, a study has been made of the mechanical properties of epoxy containing N-C and N-CC fillers. These composites were studied for their mechanical properties such as hardness, tensile, flexural and impact strength as per ASTM standards. Fraction of void cohort in the samples was quantified following the rule of mixture. Experimental results demonstrated that incorporation of N-C fillers expanded the hardness, impact strength and module of epoxy Nanocomposites. However, the tensile and flexural properties have shown declining trend for N-C/N-CC Nanocomposites. The morphological and fractographic features were examined utilizing scanning electron microscopy.

1. Introduction
Over the past few decades, engineering polymers have replaced many of the conventional materials in various applications [1,2]. This is feasible because of the benefits that polymers offer over conventional materials. In most of the engineering applications, the properties of polymers are modified using micro/Nanofillers and fibers to suit the high modulus /high strength requirements [3-5]. The principal driving forces that led to the interest and investment in polymer composite materials in the mid of 19th century were the designer’s demand for lower weight and higher rigidity for aero or space structures, electronics, sporting goods, and building structures [6-8]. In two-phase polymer matrix composites, numerous inorganic fillers with micron size inorganic particles, for example calcium carbonate, glass beads and talc have been utilized widely to upgrade the mechanical properties of polymers. Such properties can surely be custom-made by changing the volume portion, shape, and size of the filler [9,10]. The mechanical properties of the composites reinforced with micron sized functional fillers are inferior to those loaded with Nano-sized particles of a similar material. The progress of multifunctional composite materials possessing novel properties has been achieved with the incorporation of Nanofillers which has overcome numerous disadvantages of micro filler reinforced composites. Thus, such novel polymeric matrices viz., thermoset and thermoplastics reinforced with fillers having Nano-dimensions usually less than 50 nm, which are especially termed as polymer Nanocomposites (PNC’s), have attracted exceptional research interest [11-14]. Through the variation in filler dimension from micrometer to Nanometer scale, the surface area to volume ratio has been found to alter by three orders of magnitude leading to the drastic changes in morphological features as well as in their mechanical properties in polymeric matrices [15-17]. The most significant component that influences the interfacial bond is accepted to be the mechanical loading, chemical interaction and physico-mechanical boundary layers. Chemical modification of the filler surface to
improve bond has turned out to be progressively significant. From the earlier reported works, it can be concluded that to improve the filler/matrix adhesion and filler scattering surface modification of the filler is very important. Interfacial bond quality relies upon the characteristic wetting capacity of the polymer and viability of the coupling agents. Consolidation of different added substances or coupling agents in these systems helps to promote the adhesion of the matrix/filler interface and, thus, load transfer between the filler and the matrix improves the degree of filler scattering, builds the filler loading in the composite and improves the processability and mould ability. Several research groups are active in this area of research and in the most recent decade various Nano-sized fillers were presented [11-17]. Additionally, a few researchers have made endeavors to improve the mechanical and different properties of epoxy matrix by modifying Nano-calcium silicate, Nano-alumina, Nano-SiO2, Nano-TiO2, and Nano-CaCO3 [18, 19]. In the present work, the impact of Nano-clay and Nano-calcium carbonate on the mechanical properties of the composites of pristine epoxy has been researched. As far as anyone is concerned there are no genuine examinations in regards with the impact of Nano-clay and Nano-calcium carbonate on the mechanical properties of pristine epoxy yet. Hence, the purpose of this experimental work was to evaluate the effect of Nanofillers namely Nano-clay (N-C) and Nano-calcium carbonate (N-CC) on the physico-mechanical properties of epoxy Nanocomposites polymerized with conventional light-curing and additional post-curing.

2. Materials, fabrication and testing

2.1 Materials

The thermoset resin epoxy (Lapox 12) and the hardener (K6) were provided by Atul Limited, Gujarat, India. Nano-clay (N-C, size 20-30 nm) and Nano-calcium carbonate (N-CC, 20-40 nm) were purchased from Global Nano-Tech Bangalore, India. The N-C, N-CC and the epoxy resin possess Young’s modulus of 178 GPa, 69.9 GPa, and 3.35 GPa respectively and a density of 2.35 g/cm$^3$, 2.71 g/cm$^3$, and 1.15 g/cm$^3$ respectively.

2.2 Fabrication of composites

A pictorial representation of the steps involved in the fabrication of the composites has been illustrated in Fig. 1.

![Figure 1 Fabrication of N-C/N-CC epoxy Nanocomposites](image)

Epoxy resin was preheated to 60 °C before desired amount of Nano clay (N-C) / Nano calcium carbonate (N-CC) was introduced and mixed using mechanical stirrer for 20 min. To reduce the viscosity of resin/filler mix and facilitate uniform mixing, temperature was maintained at 60 °C for the whole duration of mixing using a hot plate. Further, to remove entrapped bubbles from the mixture, degassing was done for 30 min. Subsequently this mixture was ultra-sonicated for 40
min. Curing agent (K6) was added to the resin/filler mixture at 100:10 ratio and carefully hand mixed to avoid introduction of any air bubble. After, it was casted using open aluminummolds with dimensions 200 mm × 150 mm × 5 mm. The curing was done at room temperature for 24 h followed by post curing at 85 °C for 6 h. The weight percentages of N-C/N-CC were varied from 0, 1, 3 and 5 to investigate the role of Nanofillers on mechanical properties of epoxy composites.

Seven different formulations were fabricated as per the compositions summarized in Table 1. For test coupons 1N-C to 5N-C and 1N-CC to 5N-CC, the filler loading varied from 1, 3 and 5 wt. %.

2.3 Testing of epoxy Nanocomposites

2.3.1 Density test

The specimens were tested according to ASTM standards. The density of the specimens was measured in accordance with ASTM D792 with the dimension of 6mm×6mm. Equations 1 and 2 are used for calculations of theoretical density (\( \rho_{ct} \)) and void fraction (\( V_v \)) of Nanocomposites fabricated.

\[
\rho_{ct} = \frac{1}{\frac{\rho_m}{w_m} + \frac{\rho_p}{w_p}} \tag{1}
\]

where \( W \) and \( \rho \) represents weight fraction and density of the materials respectively. The suffixes \( m \) and \( p \) represent matrix and particulate respectively.

\[
V_v = \frac{\rho_{ct} - \rho_{ca}}{\rho_{ct}} \tag{2}
\]

where \( \rho_{ct} \) and \( \rho_{ca} \) represents theoretical and actual density of Nanocomposites respectively.

2.3.2 Hardness test

The hardness was measured on a Shore D hardness scale governed by ASTM D2240 with indentation of 0-2.5mm depth and 0.79 mm diameter by the application of 50 N load.

2.3.3 Tensile test

Tensile tests were carried out using universal testing machine (100 kN, Kalpak Instruments and Controls, Pune, India) at room temperature and constant crosshead speed of 10 mm/min. (Dog-bone shaped samples were made). Young’s modulus, ultimate tensile stress and elongation at break of epoxy and epoxy Nanocomposites were measured. At least 6 composite samples were tested for each composition according to ASTM standard D638-08. Equation 1 and 2 are used to calculate tensile modulus.

2.3.4 Flexural test

The flexural test was also carried out on the same instrument in obedience with ASTM D790 with a cross head speed of 10mm/min. The length to thickness ratio was kept constant and the value was 16:1. The width of the specimen was 12mm. The below equations 3, 4 are used for calculation of slope and flexural modulus. Equations 3 and 4 are used for calculations of flexural strength (\( \sigma_f \)) and flexural modulus (\( E_f \)) of Nanocomposites fabricated.

\[
\sigma_f = \frac{3FL}{2bd^2} \tag{3}
\]

\[
E_f = \frac{FL}{4ybd^3} \tag{4}
\]

where \( F \) = peak load (N), \( L \) = length of span (mm), \( y \) = deflection at peak load (mm), \( b \) = width of specimen (mm) and \( d \) = depth of the specimen (mm).

2.3.5 Impact test

Izod Impact test was conducted on a notched specimen corresponding to ASTM D256 with R1 type hammer with range of 0-2.71J on a computerized Izod impact tester. The notch was made using a notch cutter and the width of the specimen was restricted to 10.16mm. The fracture surface of the neat epoxy and their Nanocomposites was analyzed by a JEOL scanning electron microscope (SEM).
### 3. Results and discussion

#### 3.1 Measured Density

In general, the quality of composite slab fabricated, and surface hardness of a material has a great influence on its other mechanical properties. A good cast-slab of composite with hard surface of the material often results in improved mechanical properties. So, it was essential to study the influence of the Nanofillers namely, Nano-clay and Nano-calcium carbonate (N-C and N-CC), based on actual density and hardness on Epoxy. Mass density is a material property which is of prime significance in a few weight delicate applications. Density of a composite relies on the relative proportions of matrix and reinforcing materials. There is dependably a contrast between the measured and the theoretical density of a composite because of the presence of voids and pores. These voids fundamentally influence a portion of the mechanical properties and even the performance of composites. Higher void content typically means lower fatigue resistance, more prominent helplessness to water penetration and weathering. Table 1 shows the role of wt% of N-C and N-CC on the measured density of the Ep composites. The incorporation of N-C and N-CC increased the density of the Ep matrix material, verifying the usefulness of the Nanofillers as particulate reinforcement. It was found that the density of the epoxy-based composite has increased with increase in N-C or N-CC loading. The density of 5 wt% of N-C composite showed 1.74% enhancement and N-CC composite showed 1.82% enhancement in density with respect to neat epoxy. It is evident from Table 1 that the measured density and void percentage of epoxy increase with the incorporation of N-C and N-CC Nanoparticles.

| Composites | Measured density g/cm³ | Theoretical density g/cm³ | Void fraction % |
|------------|------------------------|---------------------------|----------------|
| Epoxy      | 1.152                  | 1.15                      | 0.17           |
| 1N-C       | 1.153                  | 1.156                     | 0.17           |
| 3N-C       | 1.163                  | 1.168                     | 0.43           |
| 5N-C       | 1.172                  | 1.182                     | 0.85           |
| 1N-CC      | 1.155                  | 1.156                     | 0.09           |
| 3N-CC      | 1.165                  | 1.17                      | 0.43           |
| 5N-CC      | 1.173                  | 1.184                     | 0.93           |

#### 3.2 Shore-DHardness

This has happened due to formation of agglomerations due to mechanical mixing of higher weight fraction of fillers with the matrix. The agglomeration of fillers leads to the formation of in the fabrication of Nano clay/E-glass/epoxy composites also support the results [21].Fig. 2 shows the role of the wt% of N-C and N-CC on the hardness (Shore-D) of the Ep composites. The incorporation of Nanofiller increased the hardness of the Ep composites. The hardness of the N-C filled Ep composites increased gradually with the increase of filler loading. It has been found that there is an increase of 12.5 % of hardness when N-CC was incorporated and an increase of 14.9% when N-C was incorporated. This can be explained by the fact that N-C and new generation of processed clay consists of layered silicates when stacked together is a very hard and tough material. The agglomerated Nanoparticles have resisted the indentation which is a consequence of sudden load applied on it [23].
3.3 Role of Nano fillers on tensile properties

It is evident from the plot (Fig. 3) that tensile strength, irrespective of the percentage of the fillers loaded, is lower than pristine Epoxy. N-C filler has caused a decrease in the strength by 22.2% for 5% N-C compared to neat epoxy. However, N-CC fillers have decreased the strength by 33.3% for 5% N-C composite.

The serious local plastic deformation in matrix around the particles happens during the tension deformation process. The brittle nature of epoxy makes it very sensitive to the defect sites existing
in the samples. The agglomerated structure of Nanofiller particles would act as stress concentration site when the applied stress induces the interfacial failure between particles and matrix [24]. These defects generate stress concentration sites within the matrix, resulting in decreased tensile and flexural strength.

Fig. 4 shows the variation of tensile modulus with different weight fractions of NC and N-CC. It can be observed that tensile modulus of the matrix has increased up to 23.5% for 5% N-C reinforced composite and has been constant for N-CC reinforced composite. The addition of Nanoclay reduces the flexibility of the polymer chains, which leads to the increase in young’s modulus.

3.3.1 Fractographic analysis of tensile failed specimens

According to the fractographic analysis, the rough surface and the torturous crack path on the N-C composite can be observed for both the materials. Fig. 5 shows the agglomerated particles on the crack paths of specimens.

The non-uniform distribution of particulates with agglomerations can be observed in the specimens. Fig. 6 shows the of pit formation of pit after the tensile failure of the specimen.

3.4 Role of Nano fillers on flexural properties

Flexural strength and flexural modulus were determined for the post-cured N-C/N-CC epoxy composites as per ASTM D790 standard. In general, the flexural properties of the composites are
the combined effect of tensile, compression and shear properties. High elastic fillers usually improve the flexural properties of the composites. Fig. 7 and 8 show the flexural strength and modulus as a function of N-C/N-CC filler loading respectively. From the figures it can be seen that incorporation of N-C/N-CC particles leads to reduction in flexural strength of the composites. These properties were significantly affected for higher loading of Nanofillers (> 3 wt.%). Figure 8 shows the variation of flexural modulus with different weight fractions of NC or N-CCNanocomposites. It can be observed that there is about 6% increase in the flexural modulus of N-C composite and 17.64% decrease in flexural modulus of N-CC. Further, the effect of N-C is more pronounced in enhancing the flexural modulus of epoxy compared to N-CC filled epoxy Nanocomposites. The increase in flexural modulus of N-C/epoxy Nanocomposites may be due to intercalation of Nano clay in the epoxy matrix, uniform dispersion and good interfacial adhesion that resulted in improved flexural modulus.

3.4.1. Fractographic analysis of flexural failed specimens

The qualitative evaluation of the interface property could be obtained from the fractured surface of composite materials as depicted in Figs. 9 and 10.

The SEM fractographs shown in Figs. 9 and 10 shows network of micro-cracks in the composites after the bending failure. This could be attributed to minor crack ignition and propagation in the composites because of poor bonding of Nano particles with the epoxy matrix. The micro cracks in the composites can create a larger surface area that may lead to lower flexural strength of the composites. This is expected due to weak interfacial bonding between the filler and matrix. The
The flexural modulus of composites may depend on the stiffness of high elastic modulus filler. The flexural modulus of composites is shown in Fig. 8. The flexural modulus of N-C/epoxy Nanocomposites improved by approximately 6% from 4250 MPa to 4500 MPa compared to neat epoxy. The results clearly show the effect of N-C filler enhancing the flexural modulus as depicted in fractograph in Fig. 10.

The morphology of fracture surface of N-CC flexural failed specimen has relatively less torturous paths when compared to N-C. This indicates that the resistance to crack propagation is less for N-CC and has led to greater reduction off strength of the matrix. N-C composite shows scratches and torturous paths on the fracture surface. These scratches are due to the particle peel-off from the material in which the entire Nano particle/agglomerated particles are removed from the matrix at the time of fracture. This leads to pitformation. The pit formation is observable in Fig. 10. During this process, the particles have scratched the surface and tried to resist the propagation of crack. This process has diminished the deteriorating effect of agglomerates on the flexural properties in N-C composites when compared to N-CC composites.

![Figure 9 SEM image of Flexural Failed N-C Nanocomposites](image1)

![Figure 10 SEM image of Flexural Failed N-CC Nanocomposites](image2)

3.5 Impact strength
The impact strength has considerably enhanced with increase Nano filler particles loading. Nano filler particles act as stress concentration sites, which promote cavitation at the particle-matrix boundaries during loading. The cavitation could release the plastic constraints and trigger mass plastic deformation of the matrix, leading to improved toughness. There is 62% increase in the impact energy for 5wt. % N-CC composite. There is an increase of 33.33% in impact energy for 3wt.%N-C composite. Impact strength has increased with increase in particle loading for N-CC whereas it has increased up to 3 wt. % and has decreased for further loading. The Table 2 shows
the variation of impact energy with particle loading for N-CC and N-C composites.

Table 2 Impact strength of N-C/N-CC epoxy Nanocomposites

| Composites | Impact strength (J/m) |
|------------|-----------------------|
| Ep         | 2.8                   |
| 1N-C       | 3.4                   |
| 3N-C       | 4.1                   |
| 5N-C       | 3.1                   |
| 1N-CC      | 3.8                   |
| 3N-CC      | 4.0                   |
| 5N-CC      | 7.5                   |

4. Conclusions
The mechanical properties of N-C and N-CC reinforced epoxy Nanocomposites was studied with respect to the filler loading. The following conclusions were drawn from the experimental results.

- The tensile strength and flexural strength of N-C and N-CC reinforced epoxy Nanocomposites dropped below that of neat epoxy.
- The tensile and flexural moduli of N-C reinforced epoxy Nanocomposites increased with increase in filler loading compared to N-CC reinforced epoxy and neat epoxy.
- Mechanical properties such as hardness and impact strength of N-C and N-CC reinforced epoxy Nanocomposites increased with increase in filler loading.
- Epoxy reinforced with N-CC Nanocomposites showed superior impact strength among all the composites tested.
- Finally, the results of the investigation confirmed that the mechanical properties especially hardness, tensile and flexural are better for N-C reinforced epoxy Nanocomposites compared to N-CC reinforced epoxy Nanocomposites. Incorporation of N-CC into epoxy helped in improving the impact strength of the composites.

References
[1] Hargitai, H. and Rácz, I., 2012. Applications of Macro-and Microfiller-Reinforced Polymer Composites. Polymer Composites, pp.747-790.
[2] Crawford, R.J., 1998. Plastics engineering. Elsevier.
[3] Hemanth, R., Sekar, M. and Suresha, B., 2014. Effects of fibers and fillers on mechanical properties of thermoplastic composites. Indian Journal of Advances in Chemical Science, 2, pp.28-35.
[4] Veli Deniz, NurselKarakaya and Osman G.Ersoy, (2009) Effects of fillers on the properties of thermoplastic elastomers. Society of Plastics Engineers; 01 – 04.
[5] Katz, H.S. and Mileski, J.V. eds., 1987. Handbook of fillers for plastics. Springer Science & Business Media.
[6] Njuguna, J. and Pielichowski, K., 2003. Polymer Nanocomposites for aerospace applications: properties. Advanced Engineering Materials, 5(11), pp.769-778.
[7] Shenhar, R., Norsten, T.B. and Rotello, V.M., 2005. Polymer-mediated Nanoparticle assembly: structural control and applications. Advanced Materials, 17(6), pp.657-669.
[8] Jung, Y.J., Kar, S., Talapatra, S., Soldano, C., Viswanathan, G., Li, X., Yao, Z., Ou, F.S., Avadhanula, A., Vajtai, R. and Curran, S., 2006. Aligned carbon Nanotube– polymer hybrid architectures for diverse flexible electronic applications. Nano letters, 6(3), pp.413-418.
[9] Fu, S.Y., Feng, X.Q., Lauke, B. and Mai, Y.W., 2008. Effects of particle size, particle/matrix interface adhesion and particle loading on mechanical properties of particulate–polymer composites. Composites Part B: Engineering, 39(6), pp.933-961.
[10] Selvin, T.P., Kuruvilla, J. and Sabu, T., 2004. Mechanical properties of titanium dioxide-filled polystyrene microcomposites. Materials Letters, 58(3-4), pp.281-289.

[11] Das, T.K. and Prusty, S., 2013. Graphene-based polymer composites and their applications. Polymer-Plastics Technology and Engineering, 52(4), pp.319-331.

[12] Hammel, E., Tang, X., Trampert, M., Schmitt, T., Mauthner, K., Eder, A. and Pötschke, P., 2004. Carbon Nanofibers for composite applications. Carbon, 42(5-6), pp.1153-1158.

[13] Srivastava, I., 2010. Mechanical properties of polymer Nano-composites. Rensselaer Polytechnic Institute.

[14] Gojny, F.H., Wichmann, M.H., Fiedler, B. and Schulte, K., 2005. Influence of different carbon Nanotubes on the mechanical properties of epoxy matrix composites—a comparative study. Composites Science and Technology, 65(15-16), pp.2300-2313.

[15] Suresha, B., Devarajahia, R.M., Pasang, T. and Ranganathaiah, C., 2013. Investigation of organo-modified montmorillonite loading effect on the abrasion resistance of hybrid composites. Materials & Design, 47, pp.750-758.

[16] Ray, D., Sengupta, S., Sengupta, S.P., Mohanty, A.K. and Misra, M., 2006. Preparation and properties of vinylester resin/clay Nanocomposites. Macromolecular Materials and Engineering, 291(12), pp.1513-1520.

[17] Azeez, A.A., Rhee, K.Y., Park, S.J. and Hui, D., 2013. Epoxy clay Nanocomposites—processing, properties and applications: A review. Composites Part B: Engineering, 45(1), pp.308-320.

[18] Zhang, M.Q., Rong, M.Z., Zhang, H.B. and Friedrich, K., 2003. Mechanical properties of low Nano-silica filled high density polyethylene composites. Polymer Engineering & Science, 43(2), pp.490-500.

[19] Wetzel, B., Haupert, F. and Zhang, M.Q., 2003. Epoxy Nanocomposites with high mechanical and tribological performance. Composites Science and Technology, 63(14), pp.2055-2067.

[20] Su, F.H., Zhang, Z.Z. and Liu, W.M., 2006. Mechanical and tribological properties of carbon fabric composites filled with several Nano-particulates. Wear, 260(7-8), pp.861-868.

[21] Devaraju, A. and Sivasamy, P. “Comparative Analysis of Mechanical Characteristics of Sisal Fibre Composite with and without Nano Particles”, Materials Today: Proceedings, Vol. 5 (2018), pp.14362-14366.

[22] Devaraju, A., Babu, K and Gnanavel babu, A. “Investigation on the Mechanical properties of Coconut Bunch fiber Reinforced Epoxy with Al2O3 Nano particles Composites for Structural Application”, Materials Today: Proceedings, Vol. 5 (2018), pp.14252-14257.

[23] Devaraju, A., and Pazhanivel, K. “Evaluation of Microstructure, Mechanical and Wear Properties of Aluminium Reinforced with Boron Carbide Nano Composite”, Indian Journal of Science and Technology, Vol. 9(2), pp. 1-6, 2016.

[24] Rajendran Baskaran, Muthusamy Sarojadevi and ChinnaswamyThangavel Vijayakumar, forced Plastics and Composites 2011 30: 1549 originally published online 5 October 2011.