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Synthesis, mechanical & thermal properties of clay /epoxy nanocomposites reinforced with short woven glass fiber reel

M.Ashok Kumar[1], K.Hemachandra Reddy[2], G.Ramachandra Reddy[1], Y.Venkata Mohana Reddy[3], N.Subbarami Reddy[1]*

[1]Department of Mechanical Engineering, Sri Krishnadevaraya University College of Engineering & Technology, Anantapur-515055, Andhra Pradesh, (INDIA)

[2]J.N.T.University Anantapur, Anantapur-515002, Andhra Pradesh, (INDIA)

[3]Department of Mechanical Engineering, G.Pulla Reddy Engineering College, Kurnool-518002, AP, (INDIA)

E-mail : nsramireddy@gmail.com; ashokkumarmala7@hotmail.com; koniredddy@gmail.com; rami.g.chandra@gmail.com; yvmr06@yahoo.com

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ABSTRACT

Mechanical properties viz. compression strength, comp. modulus, impact strength, and hardness are studies to assess the influence of nanoclay mixed with modified epoxy reinforced with weave glass fiber reel (WGFR). Clay/epoxy nanocomposites are prepared by high shear mechanical mixer followed by ultra-sonicator is used to obtain homogeneous mixture of epoxy and clay with the help of *in situ* polymerization. Clay is surface modified with 25-30% trimethyl stearyl ammonium. A 9 vol. % weave glass fiber is dismantled and cut in to 20 mm short lengths. Mechanical properties of nanocomposites are improved by clay addition due to improved interface between the glass fiber and epoxy. Mechanical properties are performed on (epoxy + WGFR + clay) nanocomposites as a function of clay respectively. The quantity of clay dispersed in to the epoxy system, by weight, is 0, 2, 3, 5, and 12 wt. %. Compression strength, comp. modulus, impact strength, and hardness are improved up to 5 wt % clay, degraded when clay content is further increased. Author found optimally improved mechanical properties at 5 wt. % clay content. Chemical resistance is increased significantly for all chemicals except sodium carbonate. Scanning electron microscope (SEM) is conducted on the sample fracture surfaces in order to find reasons behind the fluctuation of properties are caused due to increase in viscosity. Thermogravimetric analysis (TGA), Differential Scanning Calorimetry (DSC) experiments are performed on clay/epoxy nanocomposites reinforced with WGFR.

KEYWORDS

Epoxy;
Mechanical properties;
Montmorillonite clay;
Mechanical and thermal properties;
Woven glass fiber reel.

INTRODUCTION

Epoxy nanocomposites have simulated much interest in this new area of nanotechnology, because of the ease of manufacture and the significant gain in properties. This research shows potential for the different types

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of nanocomposites to have range of benefits from increased modulus, strength, fracture toughness, impact, compression, gas and liquid barrier properties, flame retardance and wear properties at all moderately at low concentrations of about 0.5-5% by weight[1-3]. Due to their low density of around (1.3g/cm^2) and have excellent adhesive and mechanical properties, and yet they become more promising material for high performance applications in the transportation industry, usually in the form of composite materials such as fiber composites or in honeycomb structures. In the aerospace industry, epoxy composite materials can be found in various parts of the body and structure of the military and civil air crafts with number of applications on the rise. Jin-Chein Lin[4] are studied on fabrication, characterization and fracture behavior tests under impact loading condition are performed on silica filled nanocomposites. He demonstrated that SiO_2/PA hybrid with 30 wt. % Silica is found to have the best structural stiffness among the specimens tested. Akbari et al.[5] studied on mechanical properties and deformation mechanism of epoxy/montmorillonite nanocomposites under compressive and flexural loadings are decreased due to increase in clay content. B. Qi et al.[6] studied on of DGEBA based epoxy resin with four different hardeners to shown that the addition of nanoclays can significantly improve the elastic modulus and fracture toughness of DGEBA epoxy resin, but they tend to reduce the failure strength and strain significantly with an increase of clay content level. Bo Song et al.[7] are studied on high-and low strain-rate compression experiments are conducted on epoxidized soybean oil (ESO)/clay nanocomposites with nanoclay weights of 0%, 5%, and 8%. The nanoclay is shown to have positive effects on the nanocomposites only at low strain rates. It has little or negative effects at high strain rates. Yuanqing Xiang et al.[8] are synthesized and studied on new polymer/clay nano-composite hydrogel with improved response rate and tensile mechanical properties and yet concluded that nanocomposite hydrogels had much greater equilibrium-swelling ratio, much faster response rate to pH and significantly improved tensile mechanical properties. As the content of AT increased, the tensile strength, effective cross-link chain density and glass transition temperature increased, while the equilibrium swelling ratio, deswelling rate and elongation at break decreased. Kin-tak Laua et al.[9] are showed mechanical properties improved when clay content increases with increased cluster sizes. He hence proved that hardness and cluster size go together. Yuanxin Zhou et al.[10] are studied on DMA and flexural strength hence proved that at 2 wt % clay content duo properties are optimal. Emrah Bozkurt et al.[11] studied on mechanical and thermal behavior of non-crimp glass fiber reinforced layered clay/epoxy nanocomposites and yet hence proved flexural strength and modulus are increased in accordance with increase in clay content up to 6 wt.%.

Nathaniel Chisholm et al.[12] studied on impact and compression tests in which duo properties are improved by 10-14% for later case by 20-30% for former case at 1.5wt % SiC loading and yet concluded that increase in loading degrade the mechanical properties. D.P.N. Vlasveld et al.[13] are evaluated the increased modulus of the nanocomposites offers much more support to the fibers at increased temperatures and in moisture-conditioned samples, reducing the tendency for buckling and kinking of the fibres in the composite under compression. The flexural strength of the glass fiber composites has been increased by more than 40% at elevated temperatures and the temperature at which the composites strength drops below a certain value has been increased by 40-50ºC.

This work is with reference find out optimal increase in mechanical & thermal properties, and chemical resistance on five different samples prepared by clay filled with epoxy/WGFR as function of clay. Clay dispersed by weight, is 0,2,3,5 and 12 wt %. SEM observations are conducted on the fractured surface to measure mechanical behavior besides DSC and TGA to judge weather nanocomposites are equally strong in maintaining thermal properties.

MATERIALS AND METHODS

Materials

Montmorillonite clay with surface modified with 25-30% trimethyl stearyl ammonium supplied by product of Nanocor® Inc., Aldrich, Nanoclay, Nanomer®, 1.28E from USA. Commercially available epoxy resin LY-556 & hardener HY-951 obtained from Ciba-Geigy India Ltd. Company. Weave glass fiber reel (weight: 350g/

m^2) with a thickness of 0.1mm obtained from Saint Gobain Industries Ltd., Bangalore.

Synthesis of WGFR/Clay/Epoxy nanocomposites

Firstly, clay is dried in oven at a temperature of 80°C for 24h. Then pre-calculated amount of clay and Part-A resin are mixed together in a suitable beaker. Clay is mixed with stipulated quantity of resin based on the predetermined ratio is mixed thoroughly with mechanical shear mixing for about 1h at ambient temperature conditions. Then the mixer is carried out through a high intensity ultra-sonicator for one and half hour with pulse mode (50s on / 25s off). To avoid temperature rise during the sonication process, external cooling system is employed by submerging the beaker containing the mixture in an ice bath. Once the irradiation is completed, Part-B hardener is added to the modified epoxy in the ration of 10:1 parts by weight respectively. A glass mould with required dimensions is used for making sample on par with ASTM standards and it is coated with mould releasing agent enabling to easy removal of the sample. A 9 vol. % of weave glass fiber reel is dismantled and cut with sharp scissors into 20 mm short length are used to prepare composites. In this technique a glass fiber are wetted by a thin layer of clay/epoxy suspension in a mould. Stacking of glass fiber is arranged by side by side all over the mould[14-18]. Stacking of glass fiber carefully arranged after pouring some amount of resin against the mould to keep the poor impregnation at bay. Rest of the quantity of mixture is poured over the glass fiber. Brush and roller are used to impregnate fiber. The closed mold is kept under pressure for 24 hrs at room temperature. To ensure complete curing the composite samples are post cured at 70ºC for 1 hr and the test specimens of the required size are cut out from the sheet.

Measurement of compressive strength

In the present work, the compressive strength and modulus of the epoxy/clay/nanocomposites are measured using an INSTRON (3369) Universal testing machine with a crosshead speed of 5 mm/min. The test specimens or composites are tested in accordance with ASTM D 690 standard and yet sizes of (10×10×10) mm^3. The temperature and humidity for this test are maintained at 22ºC and 45%, respectively. Six samples of each are tested and the results reported.

Measurement of impact strength test

In the present work, the impact strength of the composites is measured using an Izod impact tester. The impact test samples are made with (63.5×12.7×12.7) mm^3 dimensions using glass molds having dimensions (100×12.7×12.7) mm^3 and the notch is made according to ASTM D 256 specifications. This test is carried at ambient conditions. M/s. PSI Sales (P) Ltd., New Delhi, supplied the Izod impact tester used by the authors. In each case, five identical specimens are tested and their average load at first deformation is noted and tabulated the average value.

Hardness testing

Hardness samples are measured using a Rockwell hardness tester supplied by M/s. PSI sales (P) Ltd., New Delhi. Test specimens are made according to the ASTM D 785 (10×10×6) mm^3, the diameter of the ball indenter used is 0.25 inches and the maximum load applied is 60kg as per the standard L-scale of the tester[9]. Test surface ought to be smooth and testing carried out at room temperature. All the readings are taken 10s after the indenter made firm contact with the specimen. The test is repeated six times for every sample and the average values are tabulated.

Frictional Co-efficient test

The frictional coefficient is obtained from friction test which is performed by sliding a pin on a sample disc at 25ºC and 40% relative humidity. Before each test, the surface of counterpart pin is abraded with No. 1200 abrasive paper and cleaned with alcohol-dipped cotton, followed by drying. This friction test consisted of a rectangular nanocomposite pin sliding against nanocomposite sheets. The sliding speed of friction test is set at 0.1, 1 and 3 mm/s under a constant load of 10 N during 20 cycles. Another friction test is also performed at sliding velocity of 0.5 mm/s and the various loads used are 1, 5 and 10 N during 50 cycles. Thus the friction coefficient is measured.

Chemical resistance test

To study the chemical resistance of the nanocomposites, the test method ASTM D 543-87[9] is employed. Three acids, three alkalis and four solvents are used for this purpose. Acetic acid, nitric acid, hydro-

chloric acid, ammonium hydroxide, aqueous sodium carbonate, aqueous sodium hydroxide, carbon tetrachloride, benzene, toluene, and distilled water are used after purification. In each case, the samples (5×5×3) mm^3 are pre-weighed in a precision electrical balance and dipped in the respective chemical reagents for 24 hrs. They are then removed and immediately washed in distilled water and dried by pressing them on both sides with a filter paper at room temperature as described elsewhere[7]. The treated samples are then re-weighed and the percentage loss/gain is determined using the equation:

$$\%\ \text{weight loss or gain of the sample} = \frac{\text{Original weight} - \text{Final weight}}{\text{Original weight}} \times 100$$

Scanning electron microscopy analysis

A JEOL JSM 840A JAPAN scanning electron microscope (SEM) is used to study the morphology of fractured surfaces of nanocomposite samples at different magnifications. The fractured surfaces are gold coated initially subjecting it to SEM analysis. The scanning electron micrograms of different cross sections with different magnifications of the nanocomposite samples of (epoxy + WGFR + clay) are studied.

Thermal analysis

The thermal characteristics of the epoxy/clay binary composites are measured using both differential scanning calorimetry (DSC-2010 TA Instrument) and thermogravimetric analyses (TGA) at a rate of 10°C/min under nitrogen flow.

RESULTS AND DISCUSSIONS

Mechanical testing

To identify the optimal loading of clay, the weight fractions of clay in epoxy is varied from 0, 2, 3, 5, 12 wt. %. Mechanical tests performed on (epoxy + WGFR+ clay) as a function of clay are in accordance with ASTM standards. It can be observed in the TABLE 1, figure 1 and 2 for that the mechanical properties (i.e. compression strength, compression modulus, impact strength and hardness) of the nanophased epoxy increased continuously with increasing clay contents from 2 wt. % to 5 wt. % but decreased further increasing clay content up to 12 wt.%. Compression strength, compression modulus, impact strength and hardness properties are improved by 28.7, 103.5, 67.9, 25.7% respectively at 5 wt. % clay content, when compared over (epoxy + WGFR). In contrast with the above, properties are decreased by 36.3, 59.9, 68.6, and 34.6% respectively at 12 wt % clay content, compared over the 5 wt % clay loadings as it is observed as optimal loading. Modification of the mechanical properties of clay filled epoxy nanocomposites reinforced with weave glass fiber reel by the addition of nanoclay depends on many parameters. Adding some clay enhances the properties but adding more clay may not guarantee more improvement. This is due to the increase in viscosity of the epoxy on the addition of the clay. And the augmentation of the amount of air bubbles during mixing process.

However, it is also reasonable to believe that it should have an optimal limit since physical properties between these nanostructure materials and matrix is different. In the current experiment mechanical properties of compression strength, compression modulus, impact strength, and hardness is dropped if the amount of clay is beyond 5 wt%. Besides, for the samples with more nanoclay content, time required for solidification is also longer as well as the surface of the sample is relatively soft compared with other samples with lower nanoclay contents. We suspected nanoclays might retard the chemical reaction, and it cause incomplete curing process of the composites. For all the samples with high nanoclay content the matrix might not be fully cured. Author also found adding more clay attributes agglomeration and pull out that has been observed from the micrographs (Figure 5). At high clay content, there is a chance of agglomeration and that leads to inertia of nanoclay particle in the form of agglomeration is also increased. Figure 3 & 4 shows the variation of frictional coefficients for (epoxy + WGFR) nanocomposites as a function of clay under various sliding speed v_s load force vice versa. Figure 3 shows the variation of the frictional coefficients of (epoxy + WGFR) nanocomposites, respectively, as a function of clay content. For WGFR/nanocomposite the friction coefficient increases with an increase of force, on the other hand increased with decrease in sliding speed. The frictional coefficients of the WGFR/nanocomposites are distinctly

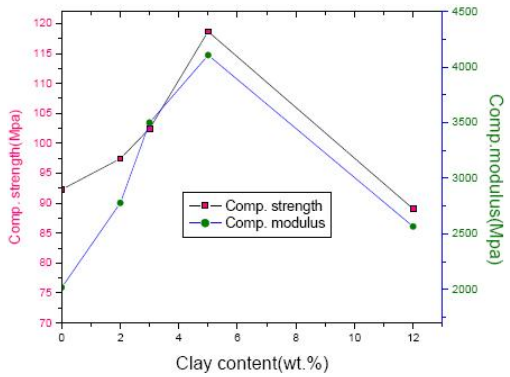


Figure 1 : Effects of modified clay contents on the comp. strength & comp. modulus of the (epoxy + WGFR) and (epoxy + WGFR + clay) nanocomposites as a function of clay respectively

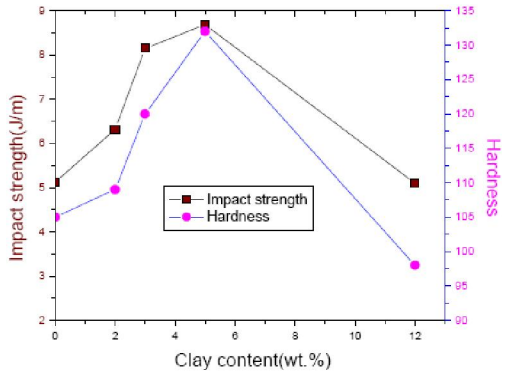


Figure 2 : Effects of modified clay contents on the impact strength & hardness of the (epoxy + WGFR) and (epoxy + WGFR + clay) nanocomposites as a function of clay respectively

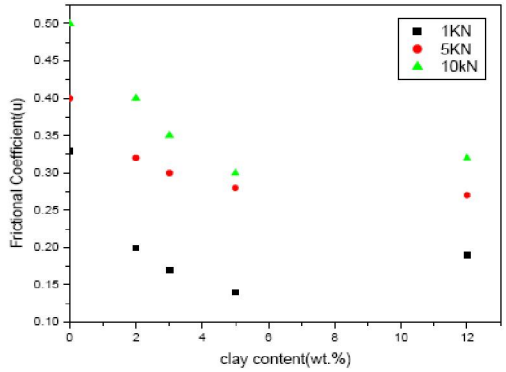


Figure 3 : Frictional coefficients as a function of clay contents after 20 cycles for clay filled epoxy nanocomposites reinforced with WGFR

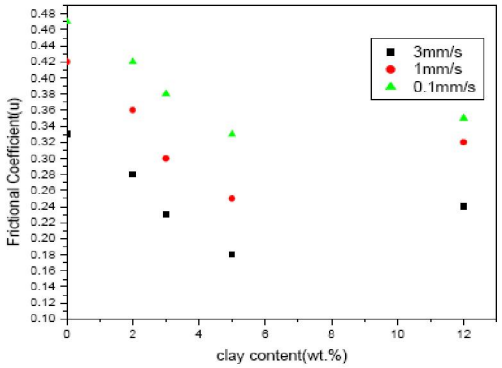
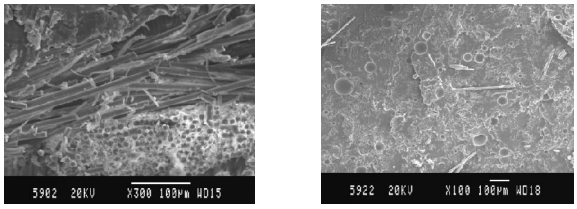


Figure 4 : Frictional coefficients as a function of clay contents after 50 cycles for clay filled epoxy nanocomposites reinforced with WGFR

TABLE 1 : Impact strength of reinforced with WGFR /epoxy/ clay nanocomposites as function of clay

Name of the sample	Comp. strength (Mpa)	Comp. modulus (Mpa)	Impact strength (J/m)	Hardness
Epoxy +WGFR	92.15	2018.32	5.12	105
Epoxy+WGFR+2wt. % clay	97.15	2778.82	6.32	109
Epoxy+ WGFR+3wt. % clay	102.43	3500.08	8.15	120
Epoxy+ WGFR+5wt. % clay	118.68	4107.30	8.60	132
Epoxy+ WGFR+12wt. % clay	87.02	2567.18	5.10	98



(a) (b)

Figure 5 : SEM micrographs of nanocomposites of 300X & 100X magnifications for (a) epoxy + 5 wt. % clay + WGFR (b) epoxy + 12 wt.% clay + WGFR as a function of clay

decreased, especially at a higher force. The lowering of the friction promotes better tribological property, is significantly shown at 5 wt% of clay content. Good reinforcement capability of clay could due to its high aspect ratio. The frictional coefficients of the nanocomposites are higher comparing at the same filler content for the nanocomposites. It is observed that the frictional coefficient considerably decreased with increasing clay loading at various sliding speeds. Moreover, the nanocomposites show better frictional resistances at larger load forces. On other the hand authors found out good frictional co-efficient values at low load force, but frictional co-efficient values are increasing with load force as shown in the figure 4. The friction resistance of the nanocomposite becomes insensitive to the increasing content of filler when the mass fraction of clay surpasses 5 wt. %.

Chemical resistance

TABLE 2 shows the weight gain (+) of weight loss

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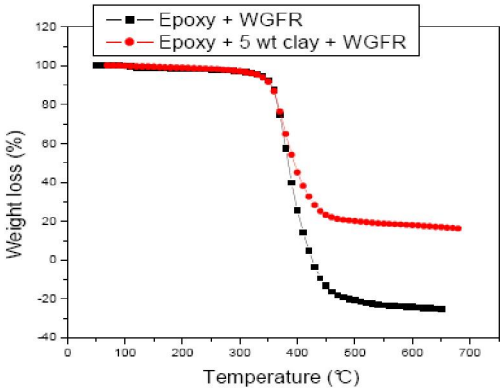

Figure 6 : TGA results of (a) epoxy + WGFR and (b) epoxy + 5 wt. clay + WGFR nanocomposites as a function of clay

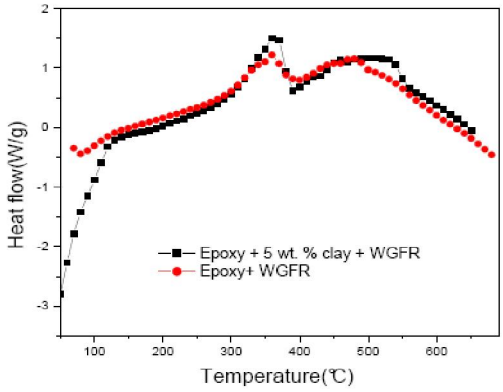

Figure 7 : DSC graphs in (a) epoxy+ WGFR (b) epoxy + 5wt% clay + WGFR nanocomposites as a function of clay

(-) experimental results of the neat epoxy and nanocomposites as a function of clay when the matrix and nanocomposites are immersed in acids, alkalis, and solvents. From the results it is clearly evident that weight gain is observed almost all the chemical reagents except sodium carbonate and toluene. The reason is attack of sodium carbons on the cross-linked epoxy. This positive value indicates that the nanocomposite materials are swollen with gel formation rather than dissolving in chemical reagents. It is also observed that, one sample is lost their weight in CCl_4. It is further observed from the table that the composite under the study are also resistant to water. This chemical resistance study clearly indicates that the clay/epoxy nanocomposites are strongly resistance to all most all chemical except sodium carbonate. The above results are suggest that these nanocomposites can be used for making water and chemical storage tanks in transportation systems in applications like aerospace, marine and rocket fuel engine systems.

TABLE 2 : Effects of chemicals on weight of pure epoxy matrix and nanocomposites at % change in weight after dipping for 24 hr

Name of the chemical	(epoxy + WGFR + clay) nanocomposites as a function of clay				
	0 wt. %	2 wt.%	3 wt. %	5 wt. %	12 wt. %
(HCl) (10%)	+1.217	+0.420	+0.255	+0.955	+1.039
(CH_3COOH) (5%)	+1.282	+0.712	+0.613	+0.559	+1.152
(HNO_3) (40%)	+2.459	+0.754	+3.940	+2.135	+2.173
(NaOH) (10%)	+1.123	+2.673	+ 0.865	+ 1.116	+0.553
(Na_2CO_3) (20%)	+0.235	-0.210	-0.190	-0.177	-0.155
(NH_4OH) (10%)	+0.919	+0.767	+ 0.431	+0.404	+0.731
Benzene	+2.380	+4.537	+10.845	+13.148	+0.537
Toluene	+2.479	-4.128	-4.955	-7.807	-3.743
CCl_4	+2.941	+5.325	+2.914	+1.459	-1.096
H_2O	+1.630	+0.773	+1.304	+1.071	+0.345

Fractured surface observations

To investigate the failure mechanism of WGFR/clay/epoxy nanocomposites, the fractured surfaces of specimens are examined. The SEM pictures of the fractured surfaces of reinforcement WGFR nanocomposites are described with 300X & 100X magnifications respectively. In figure 5a indicates increased surface roughness implies that the path of crack tip is distorted because of the glass fiber, making crack propagation more difficult. It clearly shows that in the 5 wt. % clay loading system, nanofillers are well separated and uniformly embedded in the epoxy system. In figure 5b shows pull out marks is observed as it indicate weak interface glass fiber and matrix. It also indicates high clay concentration, relatively higher fractions of clay agglomerations are observed as a result it causes micro voids which act as a stress concentration factors and facilitates shear yielding in the system and therefore, reduced mechanical properties are observed.

Thermal analysis

TGA experimental results of (epoxy + WGFR) & (epoxy + 5 wt. % clay + WGFR) nanocomposites are studied decomposition temperature. Thermogravimetric analysis is carried out to estimate the amount of resin present in the neat and nanocomposites and thermal stability. The weight loss v_s temperature in Figure 6 indicates that the as-fabricated panel contains 27 wt. % of epoxy resin and the rest is glass fiber and nanofiller. The decomposition temperatures for (epoxy + WGFR)

and (epoxy+ WGFR + clay) nanocomposites are 353°C and 356°C, respectively.

The hypothesis is examined via DSC analysis of the material used. Figure 7 illustrates the DSC graphs for (epoxy + WGFR + clay) as a function of clay. It is noticed that, there is another glass transition temperature at about 80°C lower than the main transition of the epoxy matrix. Occurrences of the second transition illustrates that there is a lower-cross link density, and even linear, epoxy present in the structure. It can be speculated that the lower T_g belongs to the chains between the silicate galleries.

CONCLUSIONS

WGFR reinforced clay/epoxy nanocomposites are prepared by high speed mechanical shear mixer & ultra-sonicator with the aid of in situ polymerization technique. Clay dispersed in the above nanocomposites by weight is 0, 2, 3, 5, and 12 wt. % clay content.

- Compression strength, compression modulus, impact strength and hardness properties are improved by 28.7%, 103.5%, 67.9%, 25.7% respectively at 5 wt. % clay content, when compared over (epoxy + WGFR).
- From TGA analysis, 3°C increase in decomposition temperature is observed for (epoxy + WGFR + clay) nanocomposites.
- From DSC analysis, it can be speculated that the lower T_g belongs to the chains between the silicate galleries.

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