Influence of organomodified nanoclay on the thermomechanical behavior of glass/epoxy nanocomposites

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Abstract - *Glass fibre-reinforced epoxy resin (GFRE) composites filled with MMT (K-10) nanomer 1.44P sigma powder were fabricated, and their mechanical and thermal properties were investigated. It is observed that with the increasing percentage of MMT (K-10) nanomer 1.44P sigma particles, there is a significant enhancement in density of the composite and void content of the composite, but there is a decline in tensile strength. Experimental results demonstrate that the GFRE composites with 3 wt% of MMT (K-10) nanomer 1.44P sigma loading show maximum density of 2.356 gm/cc with void content in percentage of 17.564%, but up to 1 wt% loading void content in percentage of 14.271% could exempted, FTIR studies in the range of wavenumber 500-4000 cm^{-1}, found OH, CH, CH_2 and CH_3 group with different stretching vibration in IR spectra, TGA and DTA studies were conducted to observe thermogram and thermal behavior of the sample.*

Key Words: *Epoxy resin, MMT (K-10) nanomer 1.44P sigma, glass fibre, hand-lay-up technique, GFRE composites.*

1. INTRODUCTION

Polymer matrix composite (PMC) materials having good thermal conductivity and mechanical strength are largely used in different areas. Properties of a composite can be improved by adding material to the matrix. Due to the properties like high specific strength, stiffness, good dielectric and resistance to corrosion of Glass fiber-reinforced polymer (GFRP) these composites are used in aerospace, automobile industries, armor, microelectronic packaging, marine, civil engineering structures, electronic circuit board, sports goods, railways etc [1-3]. Thermosetting epoxy resin based composites have many application because of its high thermal stability, low cost and moisture resistance. Due to curing of epoxy the thermal conductivity of epoxy is reduced and thermal expansion coefficient (CTE) can be increased [4]. Fused quartz or silica is used to reinforce the ceramic powder to lower the thermal expansion of epoxy to match to that of semiconductor dies and lead frames [5]. PMC contains polymer or copolymer having Nano fillers or nanoparticles dispersed in the polymer matrix.

Montmorillonite is used as nanofillers for polymer nanocomposites. It belongs to the family of 2:1 phyllosilicates and is a stretchable dioctahedral smectite. Particles of Montmorillonite are made up of aluminosilicate layers of 1nm thickness, with a regular interlayer gap. It has a large surface area of 750 m^2/g of, high aspect ratio 1:200 and low surface charge density of 0.25-0.5 equiv. mol^{-1} , because of interparticle force of attraction which help in either intercalation/exfoliation within the polymer system and successfully used to improve thermal, mechanical, barrier properties at very low loadings of <5wt% of nanofillers. So MMT-based polymer nanocomposites are widely used in aerospace, electronics, marine and automotive industries.

R. Sridhar et.al [6], the properties of degradation and moisture absorption through filler/vinylester composites in artificial seawater medium Cloisite Na is a naturally available nanoclay and Cloisite 15A an organomodified nanoclay were studied to analyze the influence of organomodification on the moisture behavior of the nanocomposites processed by using twin screw extrusion and ultrasonification, at 5 wt% of Cloisite 15A dispersion in vinylester reduces the diffusivity and permeability of the resin by 72% and 45% respectively and for the Cloisite Na at 5wt% were reduces by 33% and 71% respectively and micro hardness decreases due to the moisture diffusion of 8.68% and 16.8% respectively. T.S. Roopa et.al [7], studied the relative performance of polyester/glass and vinylester/glass laminates fabrication done by resin transfer molding and hand lay-up techniques. A resin transfer mold was fabricated and designed for preparing the laminates. Void content is less in resin transfer molding specimens than in that of hand lay-up, void content in resin transfer molding specimens was 1.4% in vinylester/glass and 0.8% in polyester/glass. Yukiko Nakahara [8], both 2 wt% clay reinforced nylon 6 and nylon 6 matrix nanocomposite were used for thermal exposure tests at temperatures of 80^{0}C, 120^{0}C and 150^{0}C respectively. N.Ragavendra et.al [9], nanoclay was originally modified by cation exchange method and distributed in vinylester using twin screw extrusion and ultrasonication using cationic surfactant HDTMA-Br. XRD shows exfoliation at 4wt% nanoclay of nanoclay/vinylester indicating that uniform distribution in the polymer. T.P. Mohan et.al [10], to study the sisal fiber reinforced polymer and the water mass uptake of nanoclay of the composites. Nanoclays at 1 wt%, 3 wt%, and 5 wt% are synthesized with the epoxy-sisal fiber composites and placed in water medium. At 5 wt% filler

filled composites the water transmission rate will decreased by three times compared to unfilled composites.

2. MATERIALS

In this work the matrix material was used as epoxy resin (Lapox L-12) and a room temperature hardener (K-6). The matrix was gives good resistance alkali's and has good adhesive property. The Glass fiber having 0.26mm thick (300GSM).

2.1 Preparation of composites

The glass-epoxy-nanoclay composite can be made from the technique of hand lay-up as shown in Fig.1 This preparation includes fibers-resin and montmorillonite nanomer 1.44p sigma. Hardener is mix in resin with montmorillonite nanomer 1.44p sigma to polymerize the polymer. Weighed quantities of room temperature curing epoxy resin-montmorillonite nanomer 1.44p sigma and hardener mix is taken and applies on the glass fabric. On this, another layer of the glass fabric was put on previous done layer and the process will be continued up required layers. The full laminate is cover with the polythene sheet and pasted on Vaseline for easy removal, for compactability was done by vacuum pump so that solid network cross-linked polymer with fiber get compacted, the vacuum pump was compress about 40 pounds per square inch so that excess resin is allow to come out. The laminate was heat at 150^0C for 2 hours in electric oven. The laminates size of (300 × 300 × 3) in mm for preparation of the fiber - resin - montmorillonite nanomer 1.44p sigma composites, fillers are made mixed with a calculated amount of epoxy.
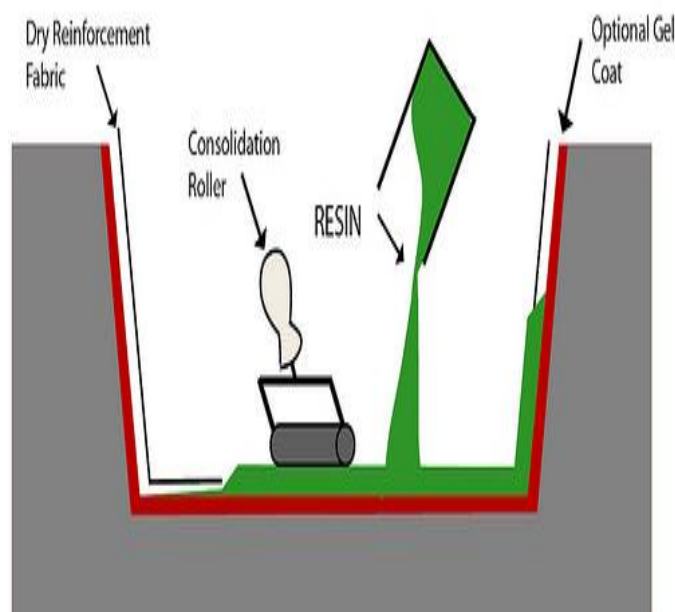

Fig.1 Hand lay-up method

The details of the composites prepared are to be shown in Table 1 provides the data of volume fraction of the composites, The table consists of composites, reinforcement material in percent volume, matrix material in percent volume and nanomer 1.44p sigma in percent volume, here there are seven different types of composites are there, 0.1% decrement in reinforcement material, matrix material was constant and 0.5% increment of the nanomer 1.44p sigma nanoparticle.

Table 1 Volume fraction of the composites.

SL NO	Composites	Reinforcement (% vol.)	Matrix (% vol.)	Nanomer (% vol.)
1	Nanomer-A	60 %	40 %	0 %
2	Nanomer-B	59.5 %	40 %	0.5 %
3	Nanomer-C	59.0 %	40 %	1.0 %
4	Nanomer- D	58.5 %	40 %	1.5 %
5	Nanomer-E	58%	40 %	2%
6	Nanomer-F	57.5%	40 %	2.5%
7	Nanomer-G	57%	40 %	3%

2.2 Experimental work

Following characterization were conducted in this work.

- Density of composites
- FTIR
- TGA
- DTA

- **Density of composites**

The composite of a density based upon correct proportion of the reinforcing, matrix materials and density is also important test to determining the properties of the laminates. The theoretical densities of the specimens are calculated from the density of nanomer-1.44p sigma, epoxy resin and E-glass fiber as 2.5, 1.29 and 2.48 g/cc, respectively. The actual density of the composite can be determined by experimentally by the simple water-immersion technique as shown in the Fig.2
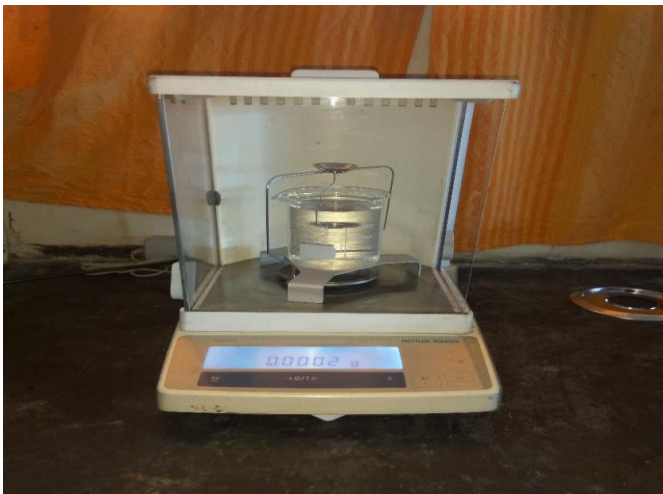
Fig.2 Water immersion technique

In water immersion technique device, the distilled water was taken into the beaker and placed on water immersion device stand, the weighing pan was dipped into the beaker and the different percentages of filler specimens are placed on the weighing pan and measured the weight in air and measured the weight in distilled water the output was taken from display in grams, using both weighs in air and water also with density of distilled water at room temperature density. The information of void content tells how the quality of the composites can be estimated. If higher the void content means lower the fatigue resistance and greater the water penetration.

- **Fourier transform infrared spectroscopy**

Fourier transform infrared spectroscopy analyses was executed using PerkinElmer instruments, with the use of nitrogen flow at a constant rate of 20 ml min^{-1}. Samples of 20-25 mg was heated about 30 to 600 ^{0}C at 10 ^{0}C min^{-1} and it was held for 4 min at 600 ^{0}C. The Fourier transform infrared spectroscopy was linked with the furnace gas transfer line. The volatiles are scanned in the range of 400-4000 cm^{-1} wavenumber range and at a resolution of about 4 cm^{-1}. The Fourier transform infrared spectra was recorded in the percentages of transmittance with the different wave number at a range 300 – 9000 cm^{-1}. The Fourier transform infrared spectroscopy as shown in Fig.3
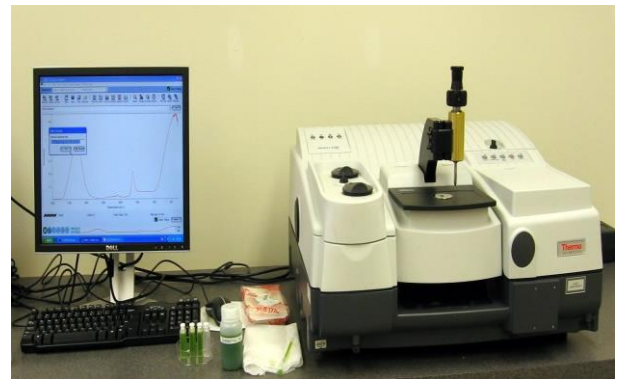

Fig.3 Fourier transform infrared spectroscopy

Using this FTIR spectroscopy we have to find how the bonding takes place and to determine the grafting of the organic modifier on the clay surface. By taking different percentages like 0%, 0.5%, 1%, 1.5%, 2%, 2.5%, 3%, of laminates powder and that powder of about 20-25mg placed in a small hole on the supporting plate after that knob will rotate and lock the hole and finally in the output will get graphs at different wave number v/s percentage in transmittance.

- **Thermal gravimetric analysis**

Figure 4 shows the TGA instrument used for thermal analysis. It is used to find the thickness of a polymer layer around the nanoparticles and also it is used to find decomposition temperature of polymer between the samples. The weight of a sample is continuously measured as a function of time and temperature. The test sample is kept in microbalance and heated in controlled condition and weight of the test sample is measured for all heating cycles. Due to change in temperature or decomposition of sample the change in weight occurs at specific temperatures. The weight loss during the decomposition of sample in experiment is due to amount of polymer that was attached to the particles in a sample.

Fig.4 Thermal gravimetric analysis

TA instrument model Q 50 was used to carry TGA at condition 25^0C to 700^0C and heating rate of $10^0C/min$ in N_2 atmosphere. Residual weight and thermal degradation behavior are analyzed and studied using TGA.

- **Differential thermal analysis**

Differential thermal analysis it is a thermoanalytic technique and it is similar to the differential scanning calorimetry. In the differential thermal analysis the study of material and an inert reference and they are made to undergo same thermal cycles, during recording any temperature between reference and sample. These differential temperatures are plotted against temperature or time. Changes takes place in the sample either in the endothermic or exothermic in nature and that can be detected relatively with the inert reference. The differential thermal analysis instrument as shown in the Fig 5



Fig 5 Differential thermal analysis

Differential thermal analysis thermogram or curve gives data of makeovers that have happened, such as crystallization, glass transitions, sublimation and melting. The area under the differential thermal analysis peak provides the enthalpy change and that is not affected from the heat capacity of sample.

3. RESULTS AND DISCUSSION

3.1 Density of composites

Graph:1 shows density of composities graph drawn between density and % of filler. In the graph Y-axis as density in gm/cc, X-axis as % of filler matrial. For 0% of filler density is 2.208gm/cc, for addition of 0.5% of nanomer 1.44p sigma the density is 2.264gm/cc, for addition of 1% of nanomer 1.44p sigma the density is 2.29gm/cc,for addition of 1.5% of nanomer 1.44p sigma the density is 2.309gm/cc, for addition of 2% of nanomer 1.44p sigma the density is 2.339gm/cc, for addition of 2.5% of nanomer 1.44p sigma the density is 2.344gm/cc, for addition of 3% of nanomer 1.44p sigma the density is 2.356gm/cc. As the % of filler content increses the density of the composites will also be increses.
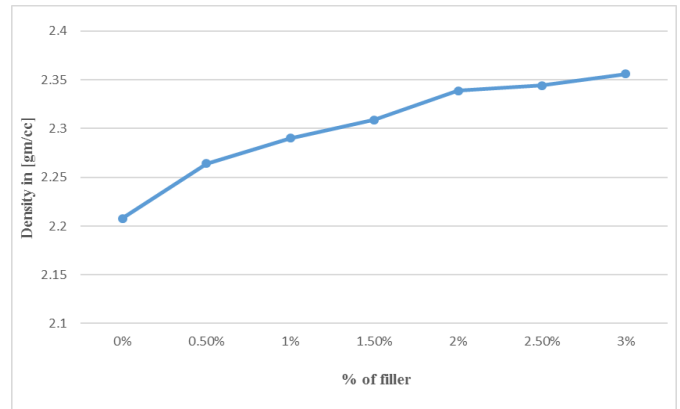
Graph:1 Density of composities

3.2 Void content in percentage

Graph: 2 shows void content in percentage graph plotted as void content in percentage verses percentage of filler. For 0% of filler material the void content will be 10.179 %, for 0.5% of filler material the void content will be 12.974 %, for 1% of filler material the void content will be 14.271 %, for 1.5% of filler material the void content will be 15.219 %, for 2% of filler material the void content will be 16.716 %, for 2.5% of filler material the void content will be 16.966 %, for 3% of filler material the void content will be 17.564 %. As the filler material nanomer 1.44p sigma increases for different seven laminates the void content in percentage also increases and important thing is only 15% of void content in acceptable because more than that laminates will formed more number of air particles so that up to 1% of filler material will be ultimate.
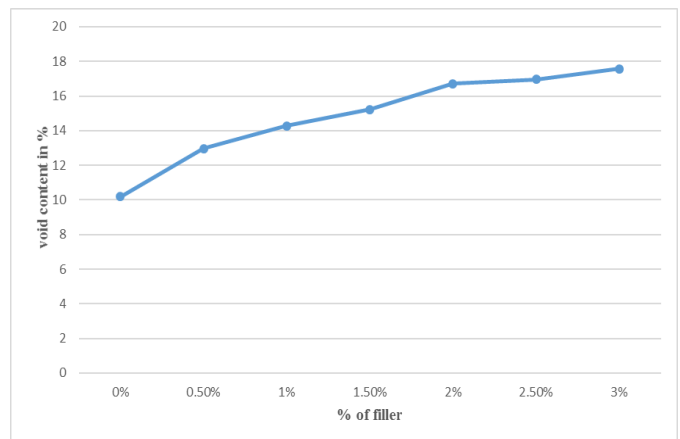
Graph.2 Void content in percentage

3.3 Fourier transforms infrared spectroscopy

Graph: 3 shows FTIR graph plotted between transmittance in % and wave number in cm^{-1}. In the graph Y-axis shows transmittance in % and X-axis shows wave number in cm^{-1}. Graph having different percentages of fillers from 0% to 3% are been added.
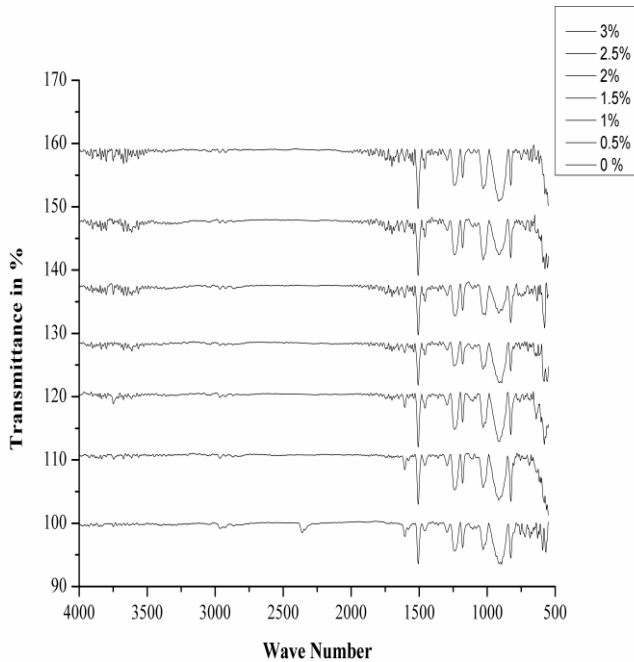

Graph: 3 Fourier transform infrared spectroscopy

FTIR graph indicates the chemical bonding and vibration of molecules present in different laminates. The peak in the area at 2900 cm^{-1} shows OH group, at 1640 cm^{-1} also indicates OH group in plane, at 2903 cm^{-1} indicates CH group in the fibre this group presence common in all composites, at 1420 and 1370 cm^{-1} indicates CH_2 and CH_3 groups in laminates, at 1240 and 690 cm^{-1} indicates epoxide ring of the epoxy resin.
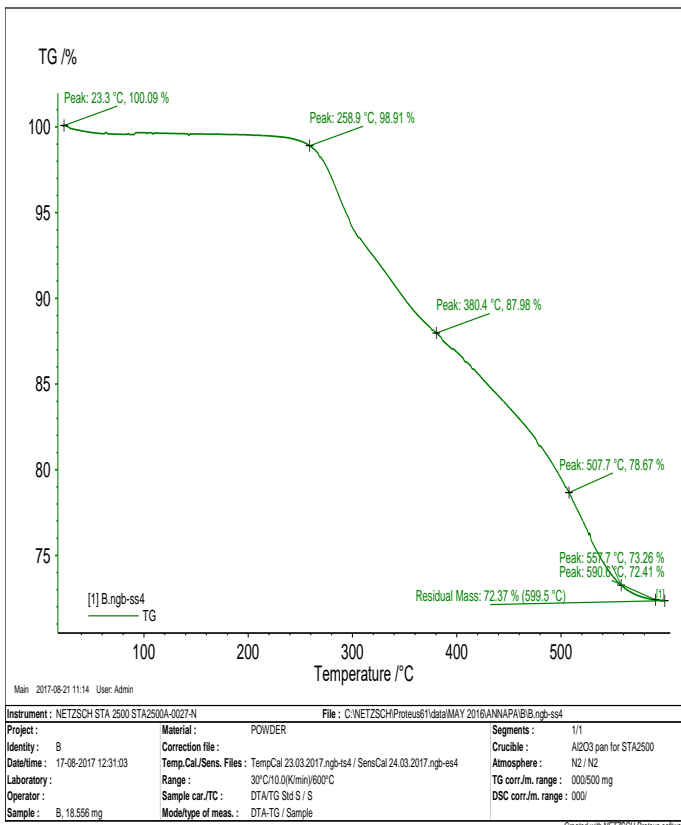
3.4 Thermo-gravimetric analysis

Graph: 4 shows TGA graph for 0% laminate. The graph plotted TG in % as Y-axis and temperature in degree Celsius as X-axis.
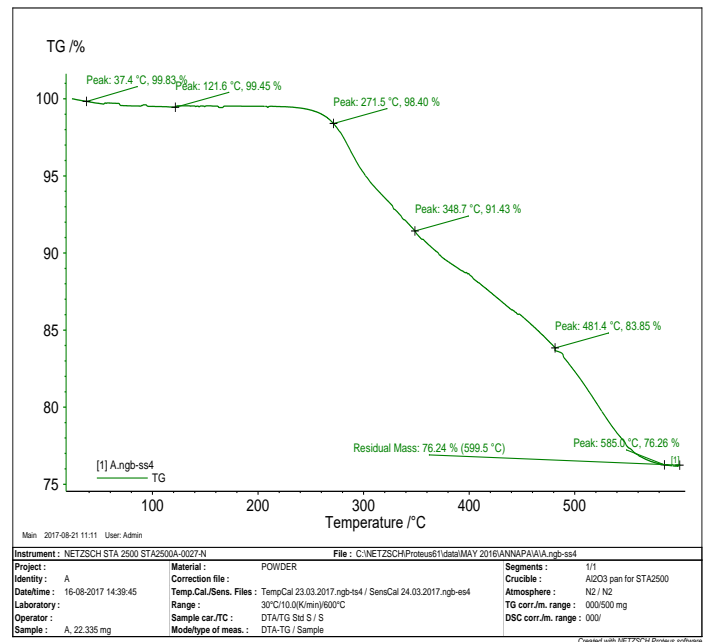
Graph: 4 TGA for 0%

The condition of this TGA experiment carried out in N_2 atmosphere, the temperature range 30^0C- 600^0C at flow rate of 10 K/min, the crucible is Al_2O_3 pan and sample was taken as 22.335 mg. At peak 99.83 % of TG the temperature will be 37.4^0C, for 99.45 % of TG the temperature will be 121.6^0C, for 98.40 % of TG the temperature will be 271.5^0C, for 91.43 % of TG the temperature will be 348.7^0C, for 83.85 % of TG the temperature will be 481.4^0C, for 76.26% of TG the temperature will be 585^0C, from the above graph shows as the temperature increases the TG will be decreased and finally the residual mass will be 76.24 % of TG at temperature 599.5^0C.
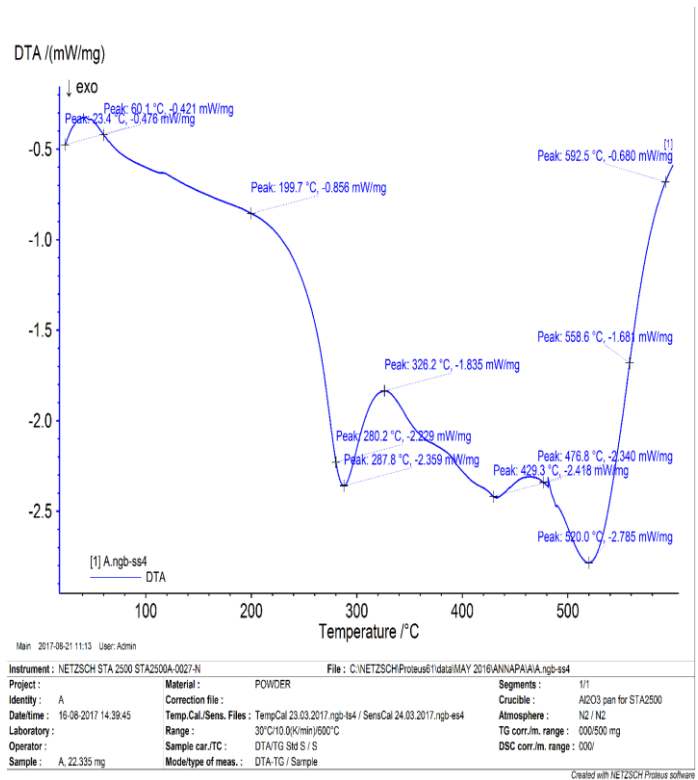
Graph: 5 shows TGA graph for 0.5 % laminate. The graph plotted TG in % as Y-axis and temperature in degree Celsius as X-axis. The condition of this TGA experiment carried out in N_2 atmosphere, the temperature range 30^0C- 600^0C at flow rate of 10 K/min, the crucible is Al_2O_3 pan and sample was taken as 22.335 mg. At peak 100.09 % of TG the temperature will be 23.3^0C, for 98.91 % of TG the temperature will be 258.9^0C, for 87.88 % of TG the temperature will be 380.4^0C, for 78.67 % of TG the temperature will be 507.7^0C, for 73.26 % of TG the temperature will be 557.7^0C, for 72.41% of TG the temperature will be 590.6^0C, from the above graph shows as the temperature increases the TG will be decreased and finally the residual mass will be 72.37 % of TG at temperature 599.5^0C.

Graph: 5 TGA for 0.5%

Graph: 6 DTA for 0%

3.5 Differential thermal analysis

Graph: 6 shows DTA graph for 0 % laminate. The graph plotted DTA in mW/mg as Y-axis and temperature in degree Celsius as X-axis. The condition of this DTA experiment carried out in N_2 atmosphere, the temperature range 30^0C-600^0C at flow rate of 10 K/min, the crucible is Al_2O_3 pan and sample was taken as 22.335 mg. At peak -0.476 mW/mg of DTA the temperature will be 23.4, for -0.421 mW/mg of DTA the temperature will be 60.1^0C, for -0.856 mW/mg of DTA the temperature will be 199.7^0C, for -2.229 mW/mg of DTA the temperature will be 280.2^0C, for -2.359 mW/mg of DTA the temperature will be 287.8^0C, for -1.835mW/mg of DTA the temperature will be 326.2^0C, for -2.418 mW/mg of DTA the temperature will be 429.3^0C, for -2.340 mW/mg of DTA the temperature will be 476.8^0C, from the above graph shows as the temperature increases, the DTA will be decreased or increased, finally the sample mass will get decreased.

Graph: 7 shows DTA graph for 0.5 % laminate. The graph plotted DTA in mW/mg as Y-axis and temperature in degree Celsius as X-axis.
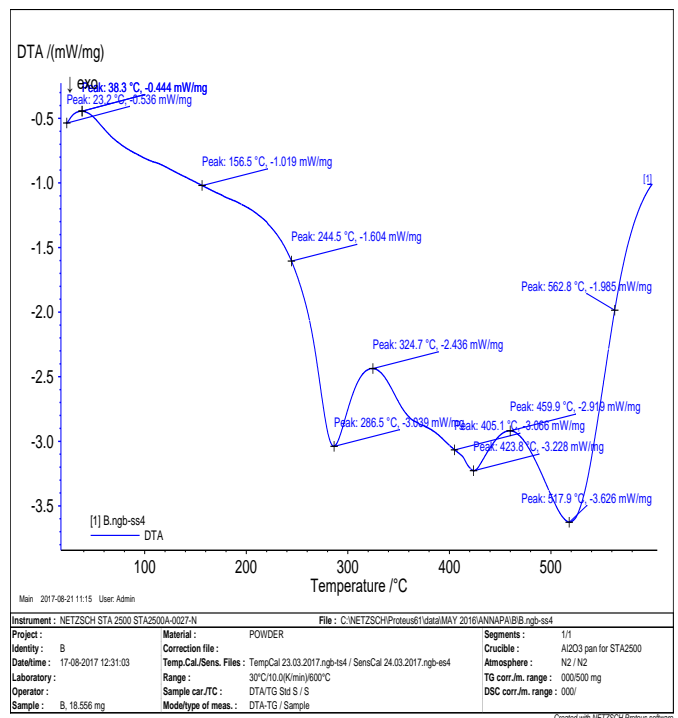
Graph: 7 DTA for 0.5%

The condition of this DTA experiment carried out in N_2 atmosphere, the temperature range 30^0C- 600^0C at flow rate of 10 K/min, the crucible is Al_2O_3 pan and sample was taken as 22.335 mg. At peak -0.536 mW/mg of DTA the temperature will be 23.2, for -0.444 mW/mg of DTA the temperature will be 38.3^0C, for -1.019 mW/mg of DTA the temperature will be 156.5^0C, for -1.604 mW/mg of DTA the temperature will be 244.5^0C, for -3.039 mW/mg of DTA the temperature will be 286.5^0C, for -2.436mW/mg of DTA the temperature will be 324.7^0C, for -2.919 mW/mg of DTA the temperature will be 459.9^0C, for -3.228 mW/mg of DTA the temperature will be 423.8^0C, from the above graph shows as the temperature increases, the DTA will be decreased or increased, finally the sample mass will get decreased.

3. CONCLUSIONS

In this present work, glass-epoxy-montmorillonite k-10 nanomer1.44p sigma nanocomposite material was selected for thermal characterization tests from tests following conclusions were made. Fabrication of glass/epoxy composites with and without nanoparticle was done using hand-layup technique.

Density and void test was carried out for different percentages of filler material with a difference of 0.5% and density and void will increase with nanomer 1.44p sigma. FTIR was carried out using IR spectroscopy instrument using the all spectra found the chemical bonding nature at different peaks of the laminates. TGA was carried out using TG instrument found the thermal behavior of the sample with the temperature. DTA was carried out using DTA instrument found the thermal behavior of the sample with different temperature for the different laminates.

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