

Study of Mechanical and Thermal Properties of Glass Fiber Reinforced Vinyl Ester Nanocomposites

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Abstract— The mechanical properties including elongation and tensile of neat vinyl ester and polymer based on layered silicate nanocomposite materials are discussed. The addition of layered silicate into the polymer matrix increased the tensile strength and young's modulus up to 06 wt. % clay loading. The incorporation of more clay resulted in decreasing the mechanical properties which was traced to the existence of aggregation layers. Likewise, up to 06 wt. % clay loading, the thermal behavior showed significant improvements and at higher clay loading the thermal pattern was reduced. The aggregation layers imparted a negative impact on the overall mechanical and thermal properties.

Keywords—Vinyl ester, nanocomposites, layered silicate, mechanical properties, thermal analysis.

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I. Introduction: -

Polymers are widely used in engineering design due to their light weight and ease of processability, however advanced engineering applications required some certain properties which are not easily found in the neat polymer. For example, thermoset polymers like vinyl ester, unsaturated polyester, & epoxy resins etc are widely utilized in different applications such as packing, automotive, marina, and insulating materials. However, the use of thermoset in thermal conductivity applications is limited which is attributed to the low thermal conductivity property. Amongst them vinyl ester resins are widely used as thermoset matrix to fabricate a variety of reinforced structures [1-8] including pipes, tanks, scrubber and ducts. They are the prime candidates for use in composite for transportation and/or infrastructure. Thus, the addition of appropriate fillers such as layered silicate can help to overcome these drawbacks [9]-[10]. The addition of the fillers to the polymer matrix was successfully reinforced in order to increase their flexibility and some other properties. The stiffness and toughness can be easily improved by the addition of such stiff fillers. In addition, the presence of the organic fillers can enlarge the thermal property like TGA. The barrier properties also can be enhanced due to the introduction of the fillers. During the last decade, the nanocomposites based on layered silicate were widely studied and attracted the industrial and academic research. The importance of these materials was traced to the unexpected properties provided compared to micro or macro composites. Due to the unexpected and enhancements in the properties as well as their famous uses, nanocomposites can be termed as a 21st century material. The particles that are used in the nanocomposites are different and depend on the properties required. Lamellar, Fibular, Tubular, and Spherical are some of the particles used in the reinforcement of the nanocomposites. The addition of Lamellar can help to provide better mechanical and barrier properties which are attributed to the shape of this particle. Likewise, strength and rigidity can be enhanced by the incorporation of Fibular. Some applications need especial care with the properties such as optical or thermal conductivity, so the addition of Spherical can meet these requirements [11].

The enhancements of the nanocomposites properties could be attributed to the high interfacial interaction between the nano fillers and the matrix as opposed to conventional composites. Layered silicate has a layer thickness in the order of 1nm and very large aspect ratio. A small amount of clay is dispersed throughout the neat polymer, thus giving a larger surface area for polymer filler interfacial interaction than in conventional composites [12], [13].

In this context, the mechanical (tensile strength & young's modulus) and thermal properties (TGA) of neat vinyl ester and the nanocomposites are investigated. Also, the effect of the addition of layered silicate into the polymer matrix on the overall properties will be analysed. In addition, the processing parameters will be evaluated and enhanced for further studies in the area of thermoset based on layered silicate nanocomposites. Glass fabric-reinforced polymer composites have found wide use for a range of structural and functional applications because of their superior performance combined with a high strength, stiffness and weight reduction. The low cost, high level of ultimate strain achievable, impact resistance, damage tolerance and gen-

eral ease of processing, high specific strength and stiffness, good formability, corrosion and fatigue resistance makes the use of glass fabric reinforcement very attractive to the aerospace and automotive industries.

II. Experimental:-

(a) Materials: - The matrix material used in this study is vinyl ester (VE) resin. "Vinyl ester resins are oligomers resulting from the reaction between bisphenol-A based epoxy oligomers and unsaturated carboxylic acids, such as acrylic or methacrylic acid, which provide unsaturated terminal sites" [6]. This material was purchased locally and commercially coded as AME 6000 T 35. Vinyl Ester resin especially formulated/branded trade mark product of Atul Ltd, Polymer Division India. An E type glass fiber (Woven roving fabric GW 123-800L5 E-glass of 803 g/m²) and S type glass fiber (Chopped strand mat) both purchased from Arvind PD Composites Pvt. Ltd. Kalol, Gujrat. The nanoclay used was organo modified clay called montmorillonite (MMT). The alkyl ammonium based clay commercial available in the trade name Garamite-1958. Garamite is an organically modified mixed clay system which is a mixture of platelets and ribbons like clay particles [Southern Clay Products. 2004]. T. Garamite 1958 is modified nanoclay and has alkyl quaternary ammonium ions on the surface of a basic bentonite clay structure. Garamite 1958 is a ribbon like structure which is found in bentonite, sepiolite and palygorskite clays and when mixed with platelets modify the rheological properties and make dispersion of the clay more easily achieved. The fibrous ribbon structure of Garamite 1958 is several microns in length and about 200 nm in width and 50 - 100A thick [Sharon Ingram. et al, 2008]. Garamate 1958 is fine powder off white in color, with specific gravity 1.5 -1.7 g/cc, having weight loss at 1000⁰ C 37 %, and having d Spacing d001 = 17.2 A⁰.

(b) Preparation of Vinyl Ester/Clay Mix: -

In order to make neat vinyl ester panels, the vinyl ester was directly mixed with the curing agent (MEKP) (mix ratio 1.5%) and then was poured in a steel mould. The mould was closed and the composite panel was left to cure at ambient temperature (20°C) for 24 hours. The vinyl ester resin was mixed with various concentrations of nanoclay at room temperature using a mechanical mixer for 1 hour. A degassing process was applied in the mixture for 3-4 hours. A curing agent (MEKP) was added to the mixture (1.5%) with further gentle mixing before transfer of the mixture to the steel mould. The mould was closed and the composite panel was left to cure at ambient temperature (20°C) for 24 hrs. A post curing process of neat and nanocomposites samples were followed at 60°C for 3 hours. The clay loadings of this fabrication lot were 0, 2, 4, 6, and 8 wt %. The clay was dried using an oven at 75⁰c for 5 hrs before being used. The Vinyl Ester/Clay composites, with different clay loading (0, 2, 4, 6, 8, Wt %) were prepared by mixing the desired amount of clay with vinyl ester resin using a mechanical stirrer at speed of 1500 rpm for 2 hrs. The hardner was added into the Vinyl Ester/Clay mixture by stiochometric ratio. The mixture was then again mixed using a mechanical stirrer by taking due care that no air bubbles are formed during stirring. This Vinyl Ester/Clay mix was then used as the matrix material for making of laminate sheets.

(c) Preparation of Vinyl Ester/GF/Clay laminate sheet:-

Vinyl Ester/GF/Clay composites sheet was prepared by hand layup technique in which two plies of (20 x 20 cm²) woven roving fabrics (WRF) and two plies of chopped strand mat (CSM) were cut. A layer of Vinyl Ester/Clay mixture was applied on a glass mold plate coated with a releasing agent. The first ply of WRF was entirely wetted by the resin mix then additional Vinyl Ester/Clay mix was added for complete wetting of second ply of CSM to be laminated. This procedure was repeated until four plies were super imposed, by taking care that the directions of fibers orientations of plies are in opposite direction of each other to form a sand-witch pattern. Then the sample was pressed with metal roller to have a thickness uniformity up to 3 to 3.2mm. Then the glass sheet was placed over the sample, & while pressing air bubbles were removed with due care. The samples were kept under press & cured at room temperature for 6 hrs. The cured composites were then cut into the proper geometry of specimens according to standards for all testing.

III. Characterization:-

A) Mechanical Properties: -

1) Tensile Strength (MPa)

Loading of clay wt %	Tensile strength MPa of VEWSCG
0	60
2	101.91
4	114.75
6	135.89
8	88.47

Table No-1:- Result of tensile strength of all Vinyl Ester/GF/Clay G.

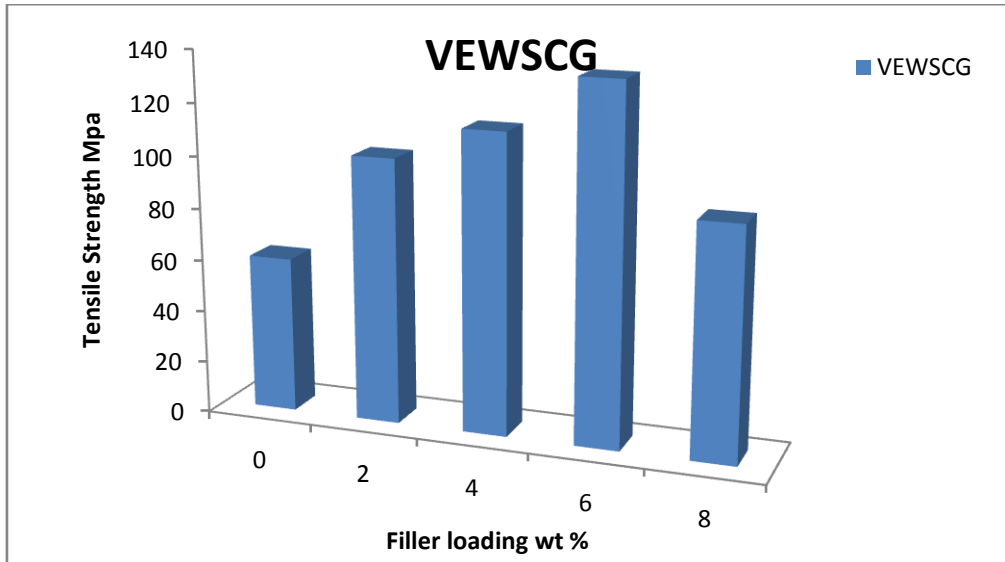


Fig No-1 Plot of tensile strength vs. clay filler loading wt %.

From Table No. 1 & Fig No. 1 it is observed that as the concentration of filler increases, tensile strength gradually increases from 2 wt % loading of clay filler and at 6% loading of clay filler value of tensile strength is highest, then drops at 8 wt % loading of clay filler, as shown in graph. This effect of filler on tensile strength may be due to the counter balance of two phenomena, first as the increased filler contents in polymer composite increases effective surface fracture energy & size of voids; it balances the agglomerations of filler particles which results in good tensile strength. Due to addition of filler to polymer matrix, a dispersed particle makes the crack propagation path longer, absorbs energy & enhances the plastic deformation. Therefore the surface fracture energy increases & the strength of composites increases with wt. % of filler. In addition the inevitably increased agglomeration above 6 wt % the dispersed filler particles results decreased in mechanical strength.

2) Impact Strength J/M: -

Loading of clay wt %	Impact Strength J/M of VEWSCG
0	985
2	1450
4	1285
6	1242
8	1222

Table No 2:- Result of impact strength of all Vinyl Ester/GF/Clay G.

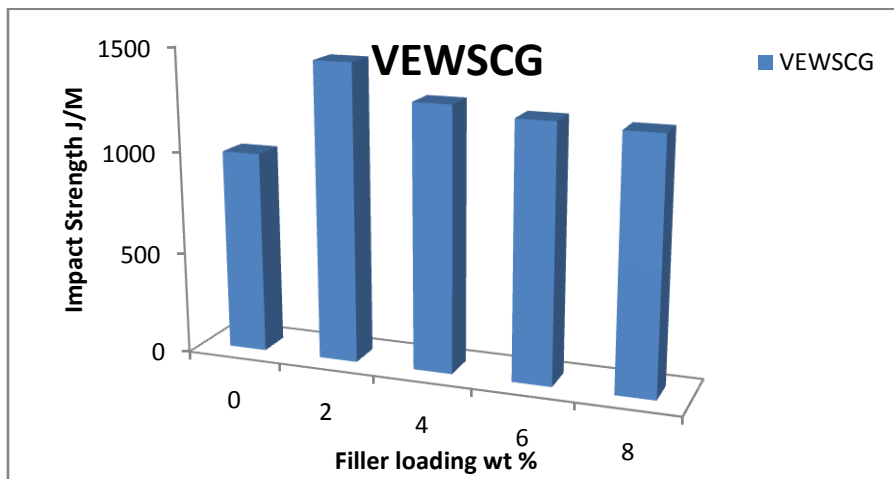


Fig No 2:- Plot of impact strength vs. clay filler loading wt %

Table No & Fig No 2 shows sudden rise in impact strength value at 2 wt % loading of clay filler, then the impact strength decreases with increase in wt % loading of filler. The impact strength in Vinyl Ester/GF/Clay Garamate composite lowers with increase in wt % loading of nanosized particles of Clay Garamate which confirms or indicates the agglomeration of lower particle size & there by generates more & more void space, which are responsible for stress propagations. The use of two types of E & S type glass fibers and the coupling agent aids to increase bonding between the filler & matrix which makes the nanocomposite with good impact strength. Thus with Garamate 1958 clay composite provides slightly low value of impact strength at 6 & 8 wt % loading of filler than 2 wt % loading of clay filler, but higher than neat vinyl ester resin value.

3) Percentage Elongations: -

Loading of clay wt %	Percentage Elongations EWSCG
0	2.75
2	10.41
4	10.69
6	8.99
8	8.79

Table No 3:- Result of percentage elongation of all Vinyl Ester/GF/Clay G

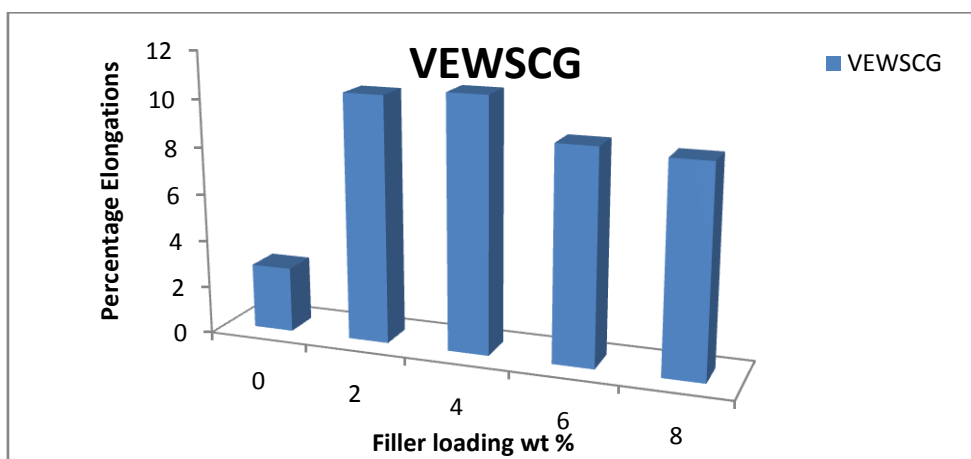


Fig No - 3 Plot of percentage elongation vs. clay filler loading wt %.

As seen from Table No & Fig No 3, a significant rise in the % elongation was seen with maximum value at 10.69 in sample with 4 wt % clay filler, this increase in % elongation may be due to orientation of two different types of glass fibers E and S used in reinforcing the matrix with help of Garamate 1958 clay. It can be observed that percentage elongation decreases drastically after 6 wt % loading of filler. The rate of decreased in elongation of break was higher due to brittleness of composite with an increase in wt % loading of clay filler. Such a significant drop could be due to the agglomeration of filler which acts as crack initiation point; this is in agreement with the general trend that elongation decreases with increasing in filler content.

4) Young's Modulus:-

Loading of clay wt %	EWSCG
0	4158
2	5616.65
4	7148.99
6	7157.13
8	6798.79

Table No.4:- Result of young's modulus of all Vinyl Ester/GF/Clay G

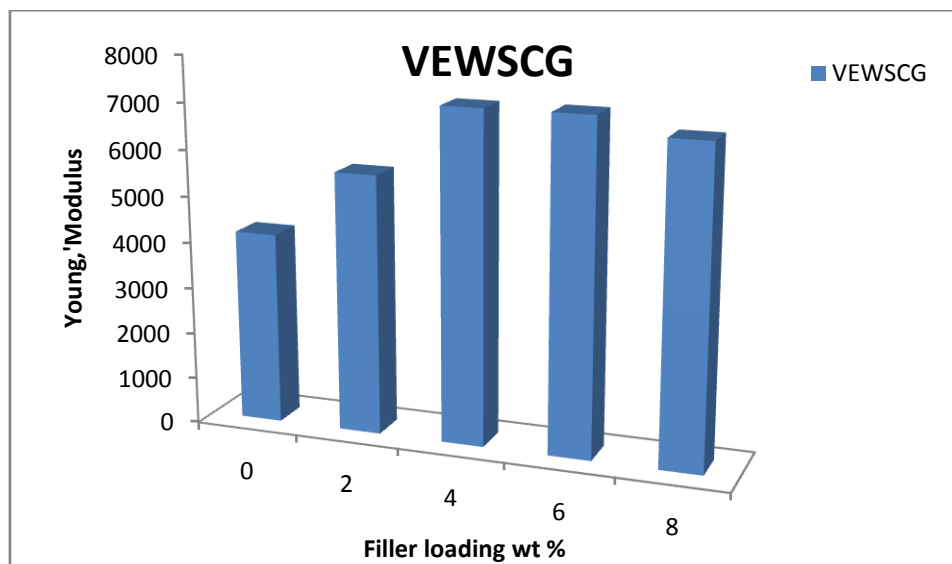


Fig No 4:- Plot of young's modulus vs. clay filler loading wt %.

Most of mechanical properties are dependent upon filler content, particle size, shape, the degree of adhesion between filler-matrix & dispersion of filler in the polymer matrix.

Young's modulus depends on the clay content. The Young's modulus increased gradually from neat sample value starting from 2 wt % loading of filler up to 6 wt % & after then it decreased, this decrease may be due to higher filler content which creates agglomeration and caused intercalation poor and makes poor adhesion or interface interaction, which decreases in Young's modulus.

The samples with Garamate 1958 clay show increase in young's modulus with the increase Garamate 1958 clay loading up to 6% & then show decrease This improvement in elastic modulus may be due to the exfoliation good dispersion of nano sized clay particles that restricts the plastic elastic deformation of polymer chains under loading as well as the good interfacial adhesion between the particles & vinyl ester matrix.

B) Thermal Properties

1) Thermo Gravimetric Analysis (TGA):-

TGA is an ideal technique to evaluate the thermal stability of final nanocomposite samples prepared and analysis of decomposition temperature of Vinyl Ester resins with various combination of loading of wt % of nanofillers and types of glass fiber. The TGA data and thermo-gram for the virgin vinyl ester and Vinyl Ester/Clay G nanocomposites are shown in Table no 6 and Figure no.6, the thermal stability of the nanocomposites was significantly enhanced by addition of clay Garamate 1958. The initial decomposition temperature (IDT) of virgin vinyl ester/glass fiber composite was 343.72°C. When Garamate 1958 clay 4 wt % was added to vinyl ester matrix, the IDT of vinyl ester/glass fiber/clay Garmate 1958 nanocomposites was 381.60°C, which was 37.88°C more than IDT of virgin vinyl ester/glass fiber composites. The final decomposition temperature (FDT) at which virgin vinyl ester i: e at which it decomposes completely i.e at T_{max}^0C 728.55°C and FDT of 4 wt % vinyl ester/glass fiber/clay Garmate 1958 nanocomposites was 735.35°C. Thus the results can be interpreted with reference to addition of clay Garamate 1958 to vinyl ester system, which increased the surface contact area between the nano clay particles and vinyl ester matrix, which in turn prevented the heat diffusion during decomposition of vinyl ester/clay g nanocomposites. The result can be attributed also to increased cross link density of the nanocomposites. The char content for the nanocomposites at 728.55°C also increased by addition of nano clay Garamate 1958. The enhancement in thermal stability is attributed to the presence of exfoliated clay platelets which hindered the diffusion of volatile decomposition products from the vinyl ester matrix. Another possible explanation for the higher thermal stability of vinyl ester/glass fiber/clay Garamate 1958 (especially for 4 wt % clay Garmate 1958) can be due to the improvement in interaction between glass fiber and vinyl ester in presence of clay Garamate 1958. Adhesion between polymer and filler particles could restrict the segmental motion of cross link near the organic-inorganic interphase (32), and therefore higher temperature is needed to breakdown the polymer network chain .However, one may found that the thermal stability of vinyl ester/glass fiber /clay Garamate 1958 composites was reduced as the loading of clay exceeds 4 wt % (i:e 6 & 8 wt%). This is related to two possible factors, i:e (i) the agglomeration of clay layered silicates , and (ii) insufficient interfacial interaction for the vinyl ester/glass fiber composites. According to Gou et al [33], intercalated dominate the structure developed at high loading of clay. The intercalated and un-exfoliated structure would reduce the thermal retardants effects because the tactoids platelets are less effective in

blocking heat. From Table no 6 we can see that the char yield of epoxy/ glass fiber/ clay Garamate 1958 4 wt % is relatively higher than that of vinyl ester/ glass fiber. This again indicates that the clay with sufficient exfoliation can act as protective barrier towards thermal degradation/decomposition by creating a tortuous path which retards the diffusion of the volatile decomposition products. Nevertheless, higher loading of clay Garamate 1958, on other hand, may promote higher thermal degradation, due to decomposition of organic modifier (alkyl ammonium ion). Also it is reasonable to mention that un- exfoliated and agglomerated clay is incable to act as effective heat protective barrier, in these vinyl ester/glassfiber/composites systems. [Ref E/C RF 8 Mohd Zulfi, Abu Bakar] All the curves show a single stage degradation pattern, vinyl ester filled with clay Garamate, shows improved thermal stability, due to addition of organically modified clay Garamate. In the vinyl ester filled with clay Garamate composites relative thermal stability and has following order Clay Garamate 1958 > Virgin vinyl ester resin.

Loading of Clay G Wt %	Initial Decomposition Temperature,(IDT) T ⁰ C	Final Decomposition Temperature,(FDT) T _{max} ⁰ C	Wt Loss %
0	343.72	728.55	35.321
2	346.72	725.03	57.344
4	381.60	735.35	41.516
6	378.9	745	87.56
8	353.32	729.34	83.203

Table No 5:-Thermal stability factors for all Vinyl Ester/GF/Clay G.

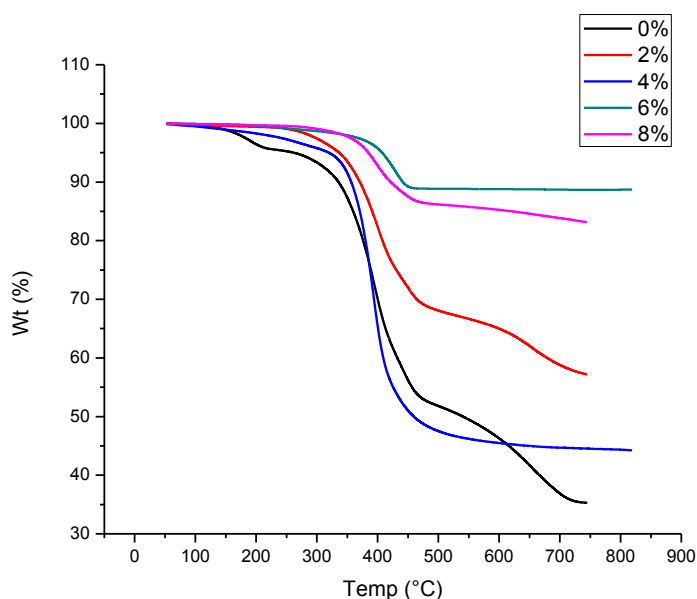


Fig No 5: - TGA thermograms of all Vinyl Ester/GF/Clay G.

(a) Virgin Epoxy,(b) 2 wt% clay G,(c) 4 wt% clay G,(d) 6 wt% clay G,(e) 8 wt% clay G
2) DMA

Loading of Clay G Wt %	Storage Modulus E'	Temperature ⁰ C	Loss Modulus E''	Temperature ⁰ C	Tan Delta	Glass Transition Temperature ⁰ C
0	7.5E+09	66.7	5.65E+08	85.2	0.4822	84.44
2	1.58E+10	65.75	4.5E+09	83.4	0.541504	83.59
4	1.3E+10	67.6	4.4E+09	83.2	0.501511	84.44
6	1.1E+10	68.9	3.4E+09	83.3	0.490835	84.23
8	1.05E+10	70.3	3.3E+09	83.95	0.469412	84.86

Table No 6: - DMA values for all Vinyl Ester/GF/Clay G.

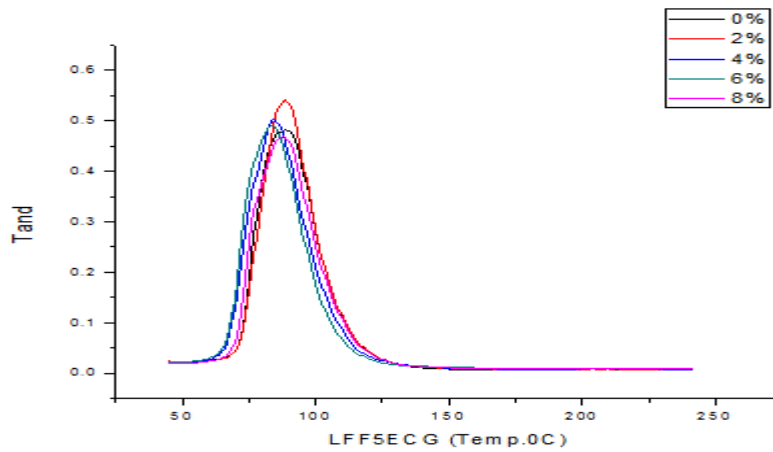


Fig No. 6:- Loss factor Vs Temperature curve for all Vinyl Ester/GF/Clay G.

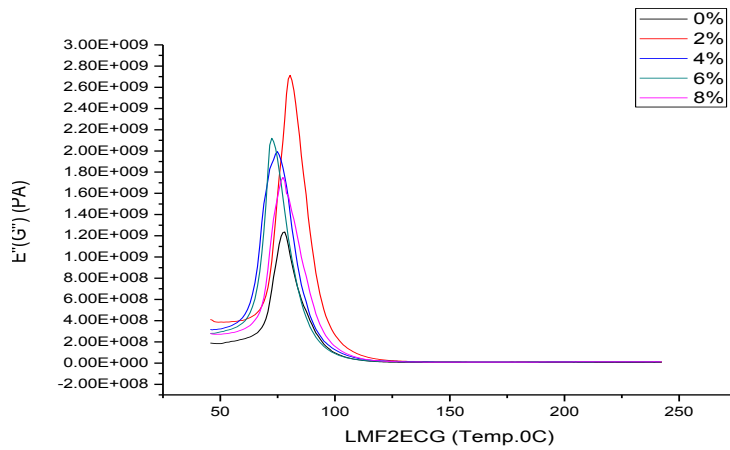


Fig No. 7:- Loss modulus Vs Temperature curves for all Vinyl Ester/GF/Clay G.

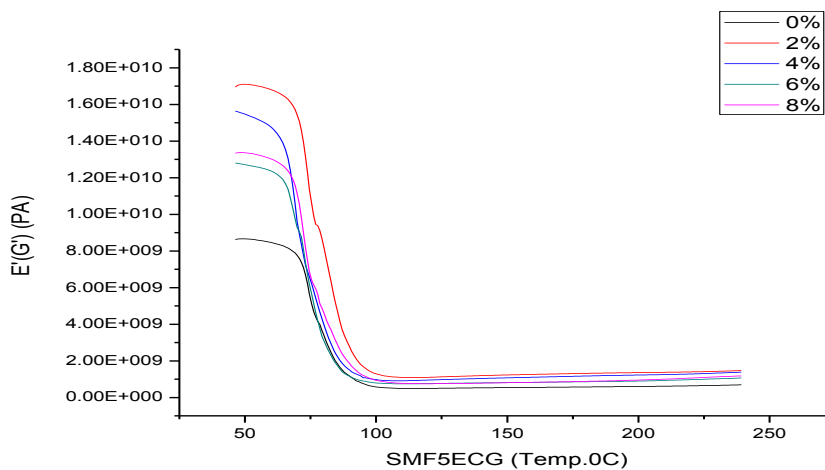


Fig No. 8:- Storage modulus Vs Temperature curves for all Vinyl Ester/GF/Clay G.

The effect of clay Garamate 1958 reinforcement on storage modulus and $Tan d$ of vinyl ester/glass fiber/clay G nanocomposites can be seen from Table No.7 in which the average values of the storage modulus (E') with different percentage weight of clay G. The E' of vinyl ester resin measured at $66.7^{\circ}C$ was $7.5E+09Pa$ and it increases, for nanocomposites monotonically with the increase in clay G content. The results obtained in this study are comparable to the literature data [14]. Table No.7 showing the values of T_g for 6 and 8 wt. % of

clay G. The measured T_g of epoxy resin was 68.9 °C for 6 wt % and 70.3 °C for 8 wt %, whereas it showed E' value 1.1E+10 and 1.05E+10 respectively. The effect of clay G loading on E' and T_g can be noticed in Figure No.8, in which the addition of clay G significantly change the glass transition temperature of the vinyl ester resin, and T_g increases by increasing nanoclay this is because movement of amorphous vinyl ester molecular chain gets hindered by finely dispersed clay nanoparticles. For the addition of 6 wt % clay G the T_g of the nanocomposite was 3° more than that of neat vinyl ester resin and whereas of 8 wt. % clay G the T_g of nanocomposite was 4° more than that of neat vinyl ester resin, so there is very slight difference between them, when completely exfoliate and disperse, it is expected to increase the T_g of polymers by restricting the molecular mobility at higher temperatures. Some authors have reported an increase in T_g [15], others have reported decreased T_g [16]. The absence of entanglement surrounding the nanoclay, the effect due to surface modifiers, unreacted resin plasticization, and a lower cross-link density have been attributed to the decrease in T_g . Table No. 7, lists the average values of Tan d for different percentage weight of clay G. It can be seen from Table No. 7, that Tan d show slight change by the addition of clay G. Various mechanisms like matrix viscoelasticity, filler/filler interfacial friction, etc., could increase the damping capacity of the polymer composite materials. However, the molecular motion at room temperature is frozen, and this may not contribute to the damping mechanisms. Table No.7 showing the list of average values of Tan d at T_g for different percentage weight of clay G. The Tan d value is higher for nanocomposites indicating the viscous damping because of the segmental motion in the polymer.

IV. Conclusion:

The mechanical and thermal properties of neat vinyl ester and the corresponding nanocomposites were investigated. The addition of layered silicate increased the tensile strength and young's modulus properties up to 6 wt. % clay loading. The incorporation of more than 6 wt. % resulted in decreasing the mechanical properties. The reduction of the nanocomposites properties even at small amounts of clay (i.e. > 6 wt.%) could be traced to the various processing parameters which include mixing time and speed, degassing process, curing method, and post curing process. Likewise, the thermal properties were enhanced by the presence of layered silicate up to 6 wt. % clay loading. Based on the parameters used in this study, 6wt. % clay loading was found to be optimal clay loading. In order to further enhancement in the mechanical and thermal properties, improvements in the preparation parameters are necessary.

References

- [1]. M.E. Kelly, P.E. In Bruins (Eds.), *Unsaturated Polyester Technology*, Gordon and Breach, New York, 1976, pp. 343-349.
- [2]. H.Y. Yeh, S.C. Yang, *J. Reinf. Plast. Compos.* 16 (1997) 414-418.
- [3]. S.S. Sonti, E.J. Barbero, *J. Reinf. Plast Compos* 15 (1996) 701-707.
- [4]. N. Hag, P. Harrison, *Corrosion Preventing and Control* 43 (1996) 162-165.
- [5]. B.P. Singh, R.C. Jain, I.S. Bharadwaj, *J. Polym Sci* 2 (1994) 941.
- [6]. K. Liao, R.I. Altkom, S.M. Mikovich, J.M. Fildes, J. Gomez, *J. Adv. Mater* 28 (1997) 54-63.
- [7]. J.R. Brown, Z. Mathys, *Compos. Part A: Appl. Sci. Manuf* 28 (1997), 675-671.
- [8]. U. Sorathia, T. Dapp, *Int. Sample Symp. Exhib.* 42 (1997) 1020-1031.
- [9]. M. Ohashi, S. Kawakami, Y. Yokogawa, and G. C. Lai, "Spherical Aluminum Nitride Fillers For Heat-Conducting Plastic Packages," *Journal of the American Ceramic Society*, vol. 88, pp.2615-2618, 2005.
- [10]. J. W. Bae, W. Kim, S.H. Cho, and S. H. Lee, "The properties of AlN- filled epoxy molding compounds by the effects of filler size distribution," *Journal of materials science*, vol. 35, pp.5907-5913, 2000.
- [11]. W. Peng, X. Huang, J. Yu, P. Jiang, and W. Liu, "Electrical and thermophysical properties of epoxy/aluminum nitride nanocomposites: Effects of nanoparticle surface modification," *Composites Part A: Applied Science and Manufacturing*, vol. 41, pp. 1201-1209, 2010
- [12]. A. I. Alateyah, H. N. Dhakal, and Z. Y. Zhang, "Processing, Properties, and Applications of Polymer Nanocomposites Based on Layer Silicates: A Review " *Advances in Polymer Technology*,. Accepted, 2013
- [13]. A. M. Youssef, "Polymer Nanocomposites as a New Trend for Packaging Applications," *Polymer-Plastics Technology and Engineering*, 2013.
- [14]. Miyagawa H., Rich M. J., Drzal L. T, 2004, Amine-Cured Epoxy/Clay Nanocomposites. II. The Effect of the Nanoclay Aspect Ratio, *J. of Poly. Sci: Part B: Polymer Physics.* 42: 391-4400.
- [15]. Messersmith P.B., Giannelis E.P. 1994. Synthesis and Characterization of Layered Silicate-Epoxy Nanocomposites, *J. Chem. Materials.* 6: 1719-1925.
- [16]. Santanu Singha, Joy Thomas M. 2009. Influence of Filler Loading on Dielectric Properties Of Epoxy-ZnO Nanocomposites, *IEEE Transactions on Dielectrics and Electrical Insulation.* 16: 531-542.

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