Mechanical and Thermal Properties Characterisation of Vinyl Ester Matrix Nanocomposites Based On Layered Silicate: Effect of Processing Parameters

A. I. Alateyah, H. N. Dhakal, Z. Y. Zhang

Abstract—The mechanical properties including flexural and tensile of neat vinyl ester and polymer based on layered silicate nanocomposite materials of two different methodologies are discussed. Methodology 1 revealed that the addition of layered silicate into the polymer matrix increased the mechanical and thermal properties up to 1 wt.% clay loading. The incorporation of more clay resulted in decreasing the properties which was traced to the existence of aggregation layers. The aggregation layers imparted a negative impact on the overall mechanical and thermal properties. On the other hand, methodology 2 increased the mechanical and thermal properties up to 4 wt.% clay loading. The different amounts of improvements were assigned to the various preparation parameters. Wide Angle X-ray Diffraction, Scanning Electron Microscopy and Transmission Electron Microscopy were utilized in order to characterize the interlamellar structure of nanocomposites.

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

I. INTRODUCTION

MANY polymers are widely used in engineering design due to their cost and ease of processability, however advanced engineering applications need some specific properties which are not easily found in the neat polymer. For example, thermoset polymers are widely utilised in different applications such as packing, automotive, marine, and insulating materials. However, the use of thermoset in thermal conductivity applications is limited which is assigned to the low thermal conductivity property. Thus, the addition of appropriate fillers such as clay can help to overcome these drawbacks [1], [2].

Polymer layered silicate nanocomposites often provide more attractive improvements to material properties than both micro and macro composite materials. The improvement can be mechanical (high strength, modulus, flexural and hardness) or thermal (thermal gravity analysis and differential scanning calorimetery) [3]. They also exhibit various properties such as decreased gas permeability and flammability, increased biodegradability and barrier properties. In addition, the incorporation of layered silicate into the polymer matrix usually results in improvement of the polymer performance. The addition of less than 5 wt.% clay into the neat matrix leads to enhance the engineering properties without sacrificing weight. The reason for enhancement of the material properties is the high amount of interfacial interaction between the organically modified layered silicate (OMLS) and the matrix, as opposed to conventional composites [2].

In this context, the investigation of the mechanical properties including tensile and flexural and thermal properties (such as TGA and DSC) of the neat vinyl ester and corresponding nanocomposites of two different methodologies took place. This study is a comparison between two earlier studies [4] and [5] in order to study the influence of the processing parameters on the mechanical and thermal properties of pristine vinyl ester and nanocomposites.

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. The layered silicate that has been used is Cloisite® 10A which is classified as a natural montmorillonite that is modified with a quaternary ammonium salt; it was purchased from Southern Clay Ltd. This clay can be used to improve different physical properties such as barrier, flame retardance and reinforcement [7].

B. Sample Fabrications Process

1. Methodology 1

Neat Vinyl Ester

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.

Nanocomposites

The vinyl ester resin was mixed with various concentrations of nanoclay at room temperature using a mechanical mixer in an ultrasonic bath for 1 hour. A degassing process was applied

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to the mixture for 2-3 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 was followed at 60°C for 3 hours. The clay loadings of this fabrication lot were 0, 0.5, 1, 1.5, 2, and 2.5 wt.%.

2. Methodology 2

Neat Vinyl Ester

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 in a hydraulic press at a temperature of 55°C and at a compaction pressure of 1 MPa for 2 hours.

Nanocomposites

Combinations of the melt intercalation method with the compression moulding method were used to fabricate nanocomposite panels. Prior to the mixing process, the layered silicate was dried for 3 hours at 120°C in a Heraeus fan-assisted oven in order to eliminate the existence of moisture. The vinyl ester resin was mixed with various concentrations of nanoclay at room temperature using a mechanical mixer in an ultrasonic bath for 2 hours. A degassing process was applied to the mixture for 3-4 hours then it was left overnight in order to get rid of the remaining air bubbles naturally. 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 in a hydraulic press at a temperature of 55°C and at a compaction pressure of 1 MPa for 2 hours. A post-curing process of the neat and nanocomposites samples followed at 80°C for 3 hours.

C. Characterisation

1. Wide Angle X-ray Diffraction (WAXD)

WAXD analysis on compression-moulded specimens was used to determine the clay intercalation and interlayer spacing utilising a Philips APD 1700 X-ray diffraction system with Cu Kα radiation (λ = 1.542A) generated at 40 mA and 40 kV. The basal-spacings (the d-spacing, in Angstroms, between layers) were calculated using Bragg's Law.

2. Scanning Electron Microscopy (SEM)

The morphology of vinyl ester /nanocomposite systems was investigated in a Hitachi S4500 SEM working at an operating voltage of 8 kV. Block faces were prepared from each material then ultrathin sections (63nm) were collected using a diamond knife in a Reichert Ultracut E ultramicrotome. Plasma etching was used to preferentially remove the vinyl ester matrix and leave the clay particles sitting proud of the surface. After adhering to SEM stubs, a thin layer of gold/palladium was applied to the specimens prior to examination in a Quanta 250 FEG SEM.

3. Transmission Electron Microscopy (TEM)

TEM measurements on vinyl ester/nanocomposite systems were performed using a high-resolution transmission electron microscope (Phillips CM12 with an associated Gatan digital camera system). Block faces were prepared from each material then ultrathin sections (63nm) were collected using a diamond knife in a Reichert Ultracut E ultramicrotome. Plasma etching was used to preferentially remove the vinyl ester matrix and leave the clay particles sitting proud of the surface.

D. Testing

1. Mechanical Testing

Flexural Test

The flexural properties (strength and modulus) of the neat vinyl ester and the corresponding nanocomposites samples were investigated by using the 3-points bending test process under the specification of BS EN 2747:1998 [8]. A span of 48 mm length was utilised in a 30 kN load cell. The load was applied midway between the supports. The speed of crosshead was 2 mm/minute. The neat and nanocomposites samples were loaded until any failure was observed and then their average values were calculated.

Tensile Test

The tensile strength and modulus of neat polymer and nanocomposites samples were carried out at a crosshead speed of 10 mm/minute under BS EN 2747:1998 [9]. The tensile test specimens were prepared by utilising a water jet into rectangular beams from the nanocomposites slabs fabricated by a compression moulding method.

2. Thermal Properties Analysis

Thermogravimetric Analysis (TGA)

TGA was performed using a TGA Q 50 V 6.1 from TA Instruments. The samples were placed in a platinum crucible, and heated in a nitrogen-filled environment at the heating rate of 20°C/min from room temperature to 600°C. The initial weights of the samples were approximately 8mg. The data from the test is displayed as TG (weight loss as a function of temperature) and as DTG (derivative thermal gravimetry, weight loss rate as a function of temperature).

III. Results and Discussion

A. Characterisations of the Interlamellar Structure and Surface Morphology

1. Wide Angle X-ray Diffraction (WAXD)

In order to study and characterise the level of intercalation and exfoliation of nanocomposites structures, the Wide Angle X-ray Diffraction (WAXD) method is widely used which can provide a quick indication of the material's structure. The nanocomposites exhibits better properties compared to conventional composites which are attributed to the sufficient dispersal of the organic fillers within a polymer sea. A micro-composite structure is observed when less interaction occurs between the layered silicate and the matrix. X-ray diffraction

is used to characterise the intercalation or exfoliation structures by calculating the basal distance (Bragg's Law) of the layered silicate, in order to identify the structure of the nanocomposite. This section will discuss the intergallery spacing of the clay powder and the nanocomposites samples of methodology 1 and 2.

Wide Angle X-ray Diffraction of Methodology 1

Table I and Fig. 1 represent the XRD values of neat clay and the corresponding nanocomposites of methodology 1. It can be seen that the addition of layered silicate into the polymer matrix increased the basal distance. The 2θ value for only Cloisite 10 A was $20°$ which indicates 0.443 nm basal distance.

The first nanocomposites sample (i.e. 0.5 wt.%) exhibits $18.60°$ which illustrates the partial intercalated d-spacing of the clay at approximately 0.477 nm with an improvement of the d-spacing about 7.67% compared to base clay. At 1 wt.% clay loading, the angle was shifted toward a lower 2θ value which was $16.95°$ and represented 0.523nm of d-spacing. By the addition of 1.5 wt.% layered silicate, the 2θ was shifted toward an upper angle and presented $19.20°$ with 0.464 basal distance. At 2 wt.% clay loading, the XRD represented a reduction of layered silicate distance compared to lower clay percentage which was 0.459 at $19.30°$. Likewise, with the presence of more clay (i.e. 2.5 wt.%) the 2θ was increased and represented $19.98°$ which was almost as same as the neat clay.

TABLE I
XRD RESULTS OBTAINED FROM DIFFERENT CLAY LOADING OF NANOCOMPOSITES OF METHODOLOGY 1 [4]

Sample No.	2θ values at 20°	The interlayer distances (nm)	d-spacing improvement %
Cloisite 10 A	20.00	0.443	00.00
VE + 0.5 wt.% clay	18.60	0.477	07.67
VE + 1.0 wt.% clay	16.95	0.523	18.05
VE + 1.5 wt.% clay	19.20	0.464	04.74
VE + 2.0 wt.% clay	19.30	0.459	03.61
VE + 2.5 wt.% clay	19.98	0.444	00.23

The improvement of the interlayer spacing at 1 wt.% was about 18.05% compared to the basal distance of base clay. This enhancement in d-spacing value at 1 wt.% indicated that the nanocomposites structure was intercalated. In addition, the enlargement of basal distance reflected a good dispersion of the layered silicate into the polymer matrix. The reduction of the basal distance by the addition of more than 1 wt.% was traced to less interaction between the clay and polymer due to insufficient mixing (time and speed) of the high viscosity. Thus, agglomeration layers were obtained in the nanocomposites structure [4].
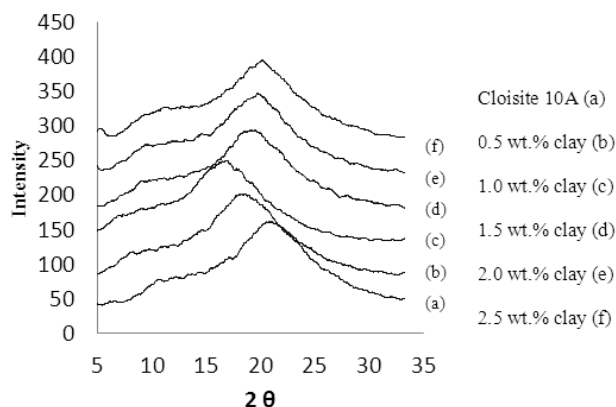

Fig. 1 XRD curve of Cloisite 10A and the corresponding nanocomposites of methodology 1 [4]

Wide Angle X-ray Diffraction of Methodology 2

From Table II and Fig. 2, it can be seen that the nanoparticles reinforced samples show various x-ray diffraction patterns. The 2θ value for only Cloisite 10 A was $20°$ which represents 0.443nm basal distance. The first peak at 2θ value of $17.12°$ (1% w/w clay reinforced sample) illustrates the partial intercalated d-spacing of the clay at approximately 0.517nm with an improvement of the d-spacing about 17% compared to base clay. At 2 wt.% clay loading, the angle was shifted toward a lower 2θ value which was $16.86°$ and represented 0.525nm of d-spacing. By the addition of 3 wt.% layered silicate, the 2θ exhibited less amount than the previous clay loading which was $16.22°$ and displayed 0.546nm of the interlayer spacing. The peak for the 4 wt.% clay loading sample at 2θ value has shifted towards a lower angle ($13.84°$) which indicated an intercalated d-spacing of 0.640nm. The improvement of the interlayer spacing at 4 wt.% was about 45% compared to the basal distance of base clay. This enhancement in d-spacing value at the 4 wt.% reinforced samples indicated that the nanocomposites structure was intercalated or partially exfoliated nanocomposites. In addition, the enlargement of basal distance reflected a good dispersion of the layered silicate into the polymer matrix. The d-spacing value of the 5 wt.% clay loading was 0.551 nm of $16.08°$ 2θ value. This reduction of 5% w/w clay reinforced sample compared to 4 wt.% clay loading was attributed to less interaction between the layered silicate and polymer due to the insufficient mixing of high viscosity mixture at high amount of clay [5].

TABLE II
XRD RESULTS OBTAINED FROM DIFFERENT CLAY LOADING OF NANOCOMPOSITES OF METHODOLOGY 2 [5]

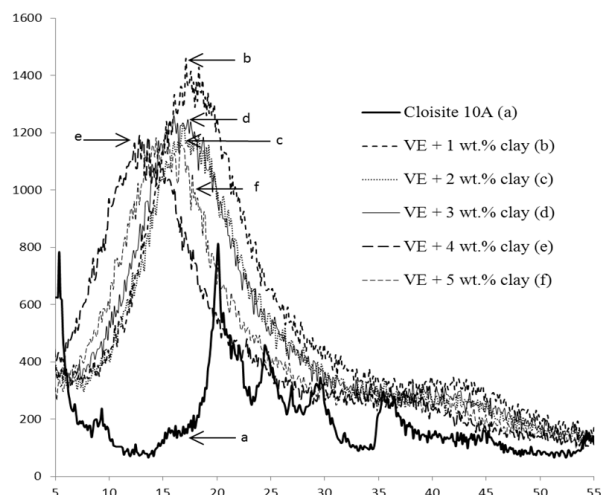| Sample No.	2θ values at 20°	The interlayer distances (nm)	d-spacing improvement %
Cloisite 10 A	20.00	0.443	00.00
VE + 1 wt.% clay	17.12	0.517	16.71
VE + 2 wt.% clay	16.86	0.525	18.51
VE + 3 wt.% clay	16.22	0.546	23.25
VE + 4 wt.% clay	13.84	0.639	44.24
VE + 5 wt.% clay	16.08	0.551	24.38

Fig. 2 XRD curve of Cloisite 10A and the corresponding nanocomposites of methodology 2 [5]

Wide Angle X-ray Diffraction Summary

In summary, a clear relationship between the layered silicate basal distance and the level of intercalation of the clay in the matrix is proved by the 2θ values. In addition, the higher the amount of interlayer distance is, the more the intercalated and partially exfoliated structure. Thus, the improvement in basal spacing led to enhancing the overall properties. As can be seen in both figures and tables, the processing parameters had a strong effect on the intercalation level of the layered silicate and the polymer matrix. In the preparation of methodology 1, the addition of more than 1 wt.% clay loading led to decrease the improvement of the distance between individual sheets of layered silicate. This indicates the existence of aggregation layers at even small amounts of clay. On the other hand, the methodology 2 samples exhibited better intercalation levels where the improvement of basal distance of layered silicate was up to 4 wt.% clay loading. In the literature, it was revealed that the optimal clay loading was to be at 4 wt.% clay loading and further additions of clay will end up having aggregation layers [10]-[12]. Thus, the methodology 2 which was followed was in close agreement to the findings of the literature.

2. Scanning Electron Microscopy (SEM)

Methodology 1

In our previous work of methodology 1 [4], the SEM images can easily show the level of distribution of the clay through the polymer as seen in Fig. 3. As the selected images show below, the largest clay agglomerates are of a similar size for the two samples, being around 30 to 35 microns in size. However, their frequency increases with increase in loading, as does the degree of infilling between them with smaller agglomerates. It can be seen that the 1 wt.% clay loading shows non-pronounced stacked layers and fairly uniform distribution. At higher amounts of clay such as 2.5 wt.%, a high number of stacked particles compared to 1 wt.% clay was observed. The results confirm the results of the XRD.
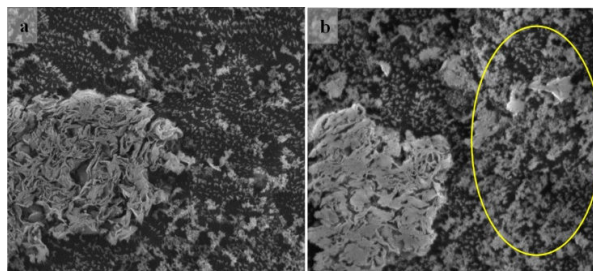

Fig. 3 SEM images at 50 µm of (a) 1 wt.% and (b) 2.5 wt.% nanocomposites [4]
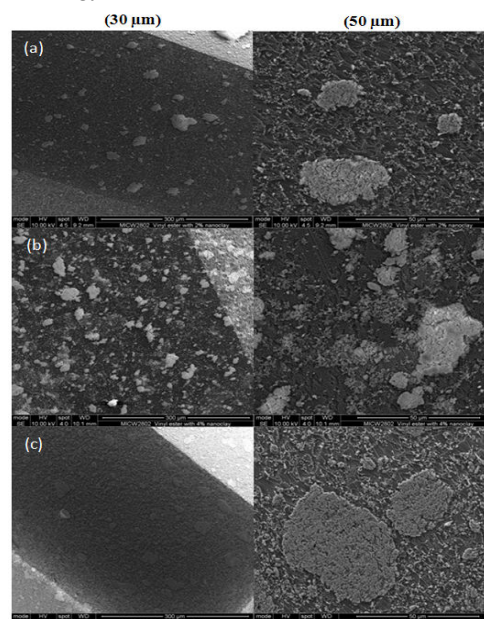
Methodology 2

Fig. 4 SEM images at 30 µm and 50 µm of (a) 2 wt.%, (b) 4 wt.% and (c) 5 wt.% nanocomposites [5]

In our previous work of methodology 2, the SEM examination in Fig. 4 shows clearly the distribution of the layered silicate through the polymer for each of the three levels of loading. The largest layered silicate agglomerates are of a similar size for all three samples, being around 30 to 35 microns in size. However, their frequency increases with enlargement in loading, as does the degree of infilling between them with smaller agglomerates. It can be seen that the 2 wt.% clay loading shows non-pronounced stacked layers and uniform distribution throughout the polymer sea. At 4wt.%, the partially intercalated / exfoliated structure is observed. The SEM image of 5 wt.% clay loading exhibited a high number of stacked clay particles compared to 2-4 wt.% clay. The results confirm the results of the XRD curves.

3. Transmission Electron Microscopy (TEM)

Methodology 1

Our previous work on the methodology 1 [4] showed that the level of dispersion of 1wt.% and 2.5 wt.% into the vinyl ester matrix are illustrated in Fig. 5. It was found that the

addition of the layered silicate into the polymer matrix was fairly homogeneous at lower clay loading (i.e. 1 wt.%), however the addition of more than 1 wt.% clay imparted the structure with agglomerative layers. In addition, it was observed that the enlarging of the clay concentrations led to increasing the clay agglomeration as the viscosity was increased. The bright region represents the matrix sea and the dark lines correspond to the stacked or individual silicate layers. At 1 wt.% clay loading, the dispersion of clay into the polymer matrix was fairly uniform and no agglomeration layers were observed. However, at 2.5 wt.%, the nanocomposites structure exhibited less homogeneity and enlarged the aggregation where additional dark areas are observed indicating the stacked silicate layers and insufficient uniform dispersion. TEM images summarised that the particles lumps are increased by the incorporation of more than 1 wt.% clay loading in this study. The results of TEM are correlated to the XRD and SEM findings.
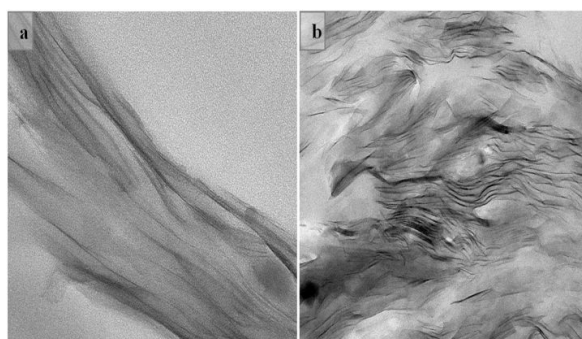

Fig. 5 TEM micrographs at 50 nm magnification of (a) 1 wt.% and (b) 2.5 wt.% nanocomposites [4]

Methodology 2

Fig. 6 shows the TEM micrographs of 2, 4, and 5 wt.% nanocomposites samples at higher magnification (20 nm), where the bright region represents the matrix sea and the dark lines correspond to the stacked or individual silicate layers. Indications are from the higher magnification images that greater levels of exfoliation of the clay particles are achieved with lower nanoclay loading. At 2 wt.% clay loading, the TEM image indicates good dispersion of layered silicate throughout the polymer matrix. An intercalated / exfoliated structure is obtained at 4 wt.% clay loading as seen in Fig. 5. The layered silicate shows uniform distribution with a few aggregation layers. At high amount of clay (i.e. 5 wt.%), additional dark areas are observed indicating the stacked silicate layers and insufficient uniform dispersion. TEM images summarise that the particles lumps are enhanced by the incorporation of more than 4 wt.% clay loading. This was traced to the high viscosity of the mixture where the ability of dispersing the clay and the polymer is restricted. It is acceptable that the higher amount of clay loading mixed with the polymer, the less exfoliated and aggregated the nanocomposites structure [2]. These findings support the results by XRD and SEM [5].
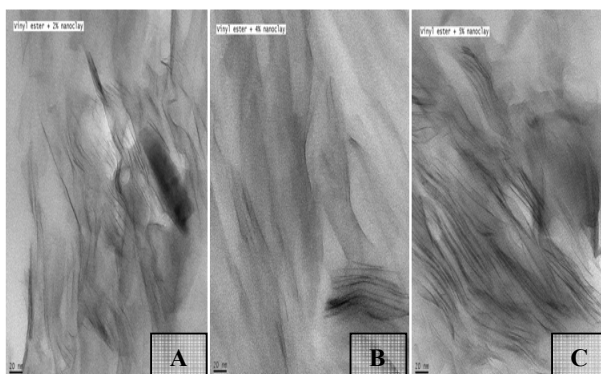

Fig. 6 TEM micrographs at 20 nm magnification of (a) 2 wt.%, (b) 4 wt.% and (c) 5 wt.% nanocomposites [5]

B. Mechanical Properties

1. Flexural Strength and Modulus

Methodology 1

The average results obtained from the five specimens tested are represented in Table III. These show a significant improvement in flexural strength and modulus for low clay concentration of nanocomposites compared to neat polymer samples.

Fig. 7 represents the relationship between the flexural strength and the clay content of the neat polymer and the corresponding nanocomposites. The flexural strength of the neat vinyl ester was 52.78 MPa whereas by the addition of only 0.5 wt.% clay loading, the strength increased up to 58.14 MPa. A further enhancement in flexural strength up to 37.33% compared to the pristine polymer was achieved by the presence of 1 wt.% clay volume which represented 72.49 MPa. At 1.5 wt.% clay loading, the strength was increased by 32.34% compared to the neat matrix; however the strength was decreased compared to 1 wt.%. A further strength reduction compared to the virgin polymer was observed by the addition of more than 1.5 wt.% ; the strength was reduced by 6.62 % and 16.96% by the addition of 2 wt.% and 2.5 wt.% clay loading respectively.

The flexural modulus followed almost the same pattern where after the addition of more than 1.5 wt.% clay the modulus was reduced as seen in Fig. 8. The significant improvement in flexural strength and modulus of the 1wt.% clay loading under the studied process parameters is attributed to the properly dispersed layered silicate within the host polymer as proved by XRD, SEM and TEM. If the parameters such as mixing time and mixer speed are increased, it can be envisaged that the optimal clay loading is from 1wt.% to higher levels. As seen in Table II, the clay had a strong influence on the resulting properties where the enhancements in flexural strength and modulus properties were proportional to the clay content up to 1 wt.% clay loading.
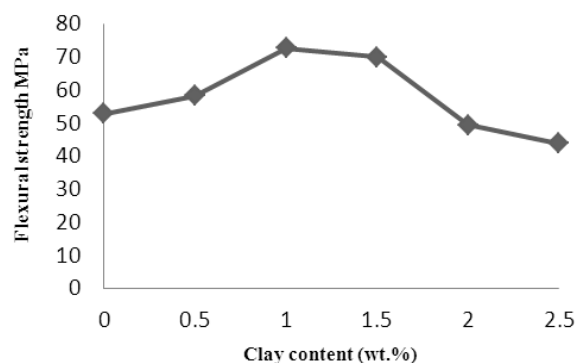
Fig. 7 The effect of clay loading on flexural strength [4]

TABLE III
FLEXURAL TEST RESULTS OF METHODOLOGY 1 [4]

Samples	Flexural	Improvement in	Flexural	Improvement in
VE	52.78	00.00	2.85	00.00
VE + 0.5	58.14	10.14	3.35	17.54
VE + 1.0	72.49	37.33	4.55	59.64
VE + 1.5	69.85	32.34	4.68	64.21
VE + 2.0	49.29	-6.62	4.39	54.03
VE + 2.5	43.83	-16.96	4.20	47.36

The improvements of the flexural properties were assigned to the shape of the layered silicate where the high aspect ratio led to high interfacial interaction within the polymer matrix. Also, it was revealed in the literature that the addition of stiff fillers can increase the flexural strength by transferring the load from the matrix to the reinforcement where the tortuous path of layered silicate plays an important role. Likewise, the stiff fillers help to improve the flexural modulus [13], [14]. In addition, the enhancement of the flexural modulus can be attributed to the restriction of the polymer chains' mobility under the status of stress. The layered silicate and polymer chains' orientations are also the key to improving the modulus property [15].
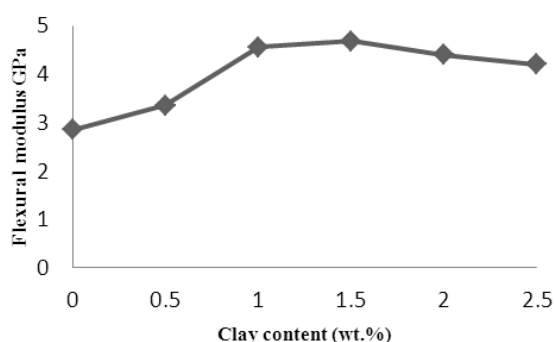

Fig. 8 The effect of clay loading on flexural modulus [4]

As can be seen, by the addition of more than 1.5 wt.% clay, the reduction of flexural properties is proportional to the clay content. The presence of aggregation layered silicate in the nanocomposites structure can be one of the reasons that influence the flexural properties where the cross-linking of the polymer chains are missed. The occurrence of aggregation layers may be related to processing parameters which includes the mixing time and speed, degassing time, and the post-curing process. As the viscosity of the mixture is increased by the addition of more clay, so the mixing time and speed was not adequate in order to disperse the layered silicate uniformly within the polymer. Also, the high viscosity mixture needs more time for degassing, otherwise the microvoids and porosity that are located in the structure will face difficulty in leaving the matrix system during the shear mixing. These voids reduce the interfacial interaction between the clay and the polymer and result in reducing the overall properties [16]-[18].

Methodology 2

The average results obtained from the four specimens tested are presented in Table IV. These show a significant improvement in flexural strength and modulus for nanocomposites compared to neat vinyl ester samples. The flexural strength and modulus for the neat sample were 56.67 MPa and 2.87 GPa, whereas for 4 wt.% clay loading the figures were 96.09 MPa and 7.05 GPa, which was an improvement of about 69.18 % and 145.35%, respectively. The significant improvement in the 4wt.% clay loading is attributed to the properly dispersed layered silicate within the host polymer as proved by XRD, SEM, EDS and TEM. As seen in the table, the layered silicate had a strong effect on the resulting properties where the improvements in flexural strength and modulus properties were proportional to the clay content up to 4 wt.% clay loading. The improvements of the flexural properties were traced to the high aspect ratio of layered silicate which had high interfacial interaction within the polymer matrix. In addition, the increment in the flexural properties can be further related to the load transferred from the matrix to the reinforcement as a result of good matrix-reinforcement adhesion. Figs. 9 and 10 elucidate the relationship between flexural strength and modulus corresponding to the clay loadings of the neat polymer and the reinforced samples.

The enhancement in flexural modulus can be related to the stiff fillers that are incorporated into the matrix which help to enhance the material's modulus [13], [14]. In addition, the layered silicate restricts the mobility of the matrix chains under load which leads to increase the modulus of the nanocomposites. Also, the modulus can be increased if the clay and matrix chains' direction is with respect to the load orientation [2], [15].

TABLE IV
FLEXURAL TEST RESULTS [5]

Samples	Flexural Strength MPa SD %	Improvement in flexural strength %	Flexural modulus GPa SD %	Improvement in flexural modulus %
VE	56.67 +/- 10.5	0.00	2.87 +/- 9	0.00
VE + 1 wt.% clay	74.16 +/- 09	30.58	4.67 +/- 7	62.34
VE + 2 wt.% clay	80.40 +/- 8.5	31.82	4.89 +/- 5	70.15
VE + 3 wt.% clay	85.37 +/- 4	42.35	5.07 +/- 5	76.29
VE + 4 wt.% clay	96.09 +/- 5	69.18	7.05 +/- 4	145.35
VE + 5 wt.% clay	69.60 +/- 10.7	22.55	4.75 +/- 8	65.21

As can be seen from Table II, at higher clay reinforcement, i.e. 5 wt.%, both strength and modulus have been reduced. The reduction of both strength and modulus of the 5wt.% clay loading may be related to the existence of aggregation layered silicate in the nanocomposites structure which imparts a negative effect on the overall cross-linking properties as seen in SEM, EDS and TEM. The reason for the agglomeration could be because of the mixing parameter, i.e. the length of time for the mixing may not have been adequate, as the volume of layered silicate was increased. Moreover, as the clay loading increases, the viscosity of the nanocomposites get increased as a result; at higher clay loading, insufficient degassing will be obtained. Thus, the microvoids and porosity that are located in the structure will face difficulty in leaving the matrix system during the shear mixing. As a result, less interfacial interaction between the polymer and layered silicate will be present [16]-[18]. The improvement in flexural properties in the nanocomposites samples in this study is in close agreement to the study that was undertaken by Kodgire et al. [19].
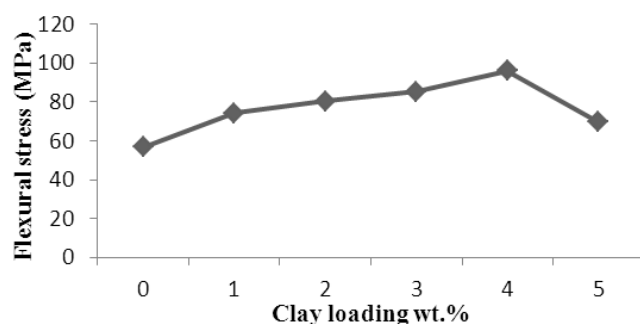

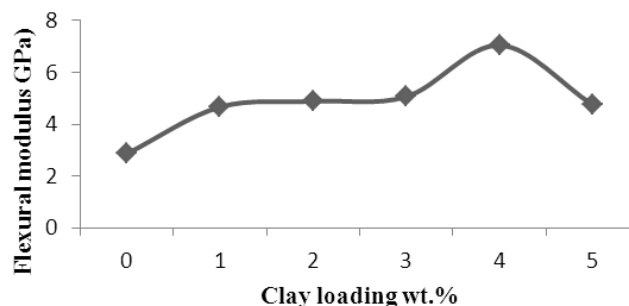Fig. 9 The effect of clay loading on flexural strength [5]

Fig. 10 The effect of clay loading on flexural modulus [5]

2. Tensile Strength and Modulus

Methodology 1

Five specimens in each loading were tested and the averages of those values were extracted and calculated from the tensile curve and are presented in Table V. As seen in Table V, the enhancement of the amount of tangent modulus for nanocomposite samples compared to the pristine one was observed. The clay loading had a strong effect on the tangent modulus as the results were enhanced by the presence of layered silicate. The neat polymer represented 1.08 GPa. By the addition of only 0.5 wt.% clay, the tangent modulus was increased by 6.48% compared to the neat polymer and showed 1.15 GPa. Further enhancement in the tangent modulus was observed by the incorporation of 1 wt.% clay loading where the modulus was increased up to 1.30 GPa. At 1.5 wt.% clay, the modulus was almost the same as 1 wt.% and represented 1.29GPa. The addition of more clay led to decreasing the tangent modulus as the examples of 2 wt.% and 2.5 wt.% showed. Fig. 11 illustrates the relationship between the tangent modulus and clay content. Fig. 12 represents the effect of clay content on the ultimate tensile strength.

TABLE V
TENSILE TEST OUTCOMES FOR NEAT AND DIFFERENT CLAY LOADING SAMPLES [4]

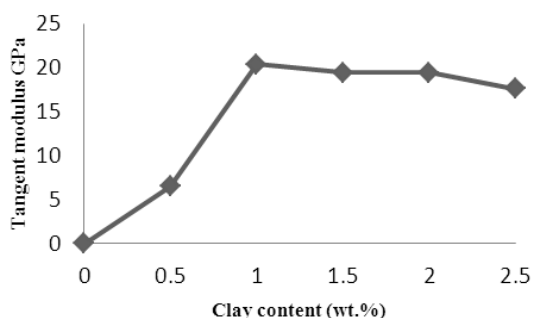| Samples	Tangent modulus GPa SD %	Improvement in Tangent modulus %	Ultimate tensile strength MPa SD %	Improvement in UTM strength %
VE	1.08 +/- 11	0	13.05 +/- 18	0.00
VE + 0.5 wt.% clay	1.15 +/- 14	6.48	16.91 +/- 14	29.57
VE + 1.0 wt.% clay	1.30 +/- 10	20.37	19.01 +/- 11	45.67
VE + 1.5 wt.% clay	1.29 +/- 9	19.44	18.50 +/- 7	41.76
VE + 2.0 wt.% clay	1.29 +/- 4.5	19.44	18.11 +/- 9	38.77
VE + 2.5 wt.% clay	1.27 +/- 7	17.59	16.81 +/- 13	28.81

Fig. 11 The tangent modulus improvements at different clay loading levels [4]
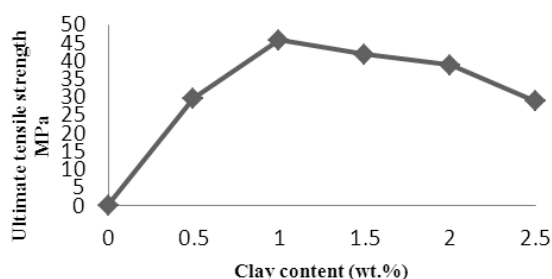

Fig. 12 The tensile properties improvements of neat polymer and nanocomposites [4]

Methodology 2

Four specimens in each loading were tested and the averages of those outcomes were obtained and are presented in Table VI. Table VI and Fig. 13 represent the enlargement of the amount of tangent modulus for nanocomposite samples compared to the pristine one. The clay loading had a strong influence on the tangent modulus as the results were increased by the addition of nanoparticles. For example, 4wt.% layered silicate represents the highest amount of tangent modulus and was increased by up to 43 % compared to the property of the host matrix.

TABLE VI
TENSILE TEST OUTCOMES FOR NEAT AND DIFFERENT CLAY LOADING SAMPLES [5]

Samples	Tangent modulus GPa SD %	Improvement in Tangent modulus %	Ultimate tensile strength GPa SD %	Improvement in UTM strength %
VE	1.19 +/- 11	0	12.53 +/- 6	0.00
VE + 1 wt.% clay	1.22 +/- 14	2.52	17.28 +/- 7	37.90
VE + 2 wt.% clay	1.46 +/- 10	22.68	18.99 +/- 9	51.56
VE + 3 wt.% clay	1.59 +/- 9	33.61	19.16 +/- 8	52.91
VE + 4 wt.% clay	1.70 +/- 4.5	42.87	27.96 +/- 5	123.14
VE + 5 wt.% clay	1.55 +/- 7	29.68	20.74 +/- 4	65.52

Fig. 14 shows the relationships between the loading levels of layered silicate and ultimate tensile strength (UTM). The nanocomposite sample shows a significant improvement with the comparison to neat polymer. By adding just 1% clay, the tensile strength was increased up to 38%. 123% improvement in UTM was observed by incorporation of only 4wt.% layered silicate loading. The reasons for the properties' improvements were discussed in Section I *A*.

The effect of clay reinforcement on the elongation behaviour of polymer nanocomposites has not been widely studied. The elongation is normally reduced with the addition of nanoparticles such as MMT on polymers [20]-[22]. The elongation is a sign to measure the ductility of the material. There is a small improvement in the elongation with 2wt.% clay loading which may be attributed to the conformational effect at the layered silicate-polymer interface. Other nanocomposites samples had a marginal reduction of the elongation, up to 4wt.% clay loading.
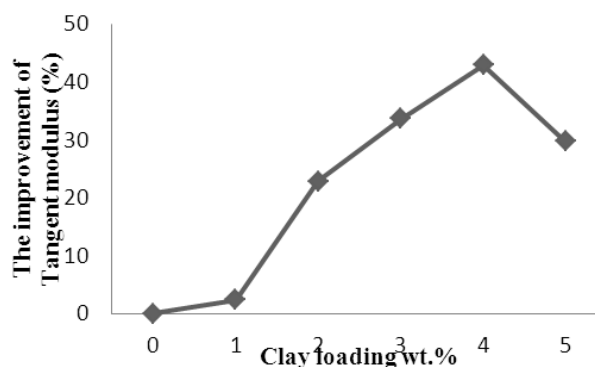

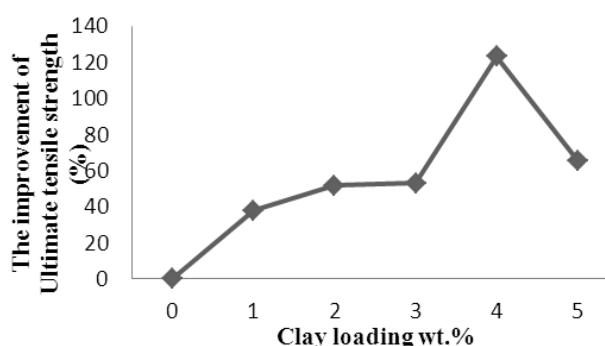Fig. 13 The improvement amount of tangent modulus for different clay loadings [5]

Fig. 14 The improvement of tensile strength properties of neat polymer and nanocomposites [5]

3. Mechanical Properties Summary

The above tables conclude that the processing parameters had a strong effect on the mechanical properties. The flexural modulus and strength of methodology 1 were improved up to 1 wt.% clay loading. Further addition of layered silicate resulted in decreasing the properties which was ascribed to the

presence of the aggregation layers where the stress concentration factor was high. When the stress concentration factor is high, the initiation of premature failure may happen. In addition, at high clay loading, the existence of high amounts of microvoids was in place which reduced the interfacial interaction between the polymer and layered silicate. On the other hand, methodology 2 represented better improvements in both flexural strength and modulus where the enhancements were up to 4 wt.% clay loading.

The improvements of the flexural properties in methodologies 1 and 2 were traced to the high aspect ratio of layered silicate which had high interfacial interaction within the polymer matrix. In addition, the increment in the flexural properties can be further related to the load transferred from the matrix to the reinforcement as a result of good matrix-reinforcement adhesion. The tensile properties followed the same pattern as the flexural properties.
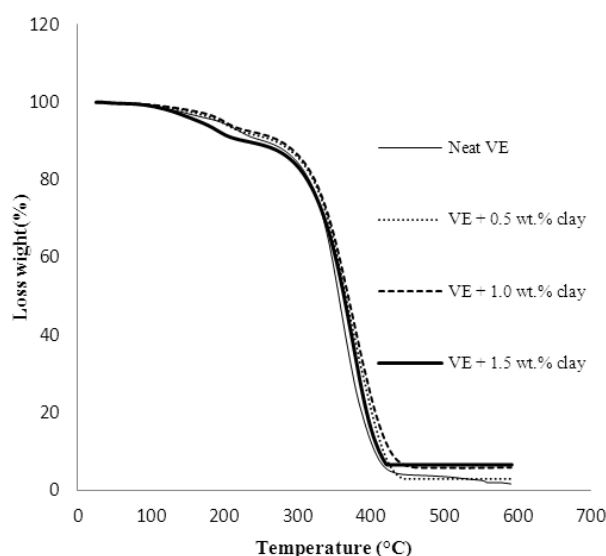

Fig. 15 TGA curve of neat VE and corresponding nanocomposites [4]

C. Thermal Properties

1. Thermogravemetric Analysis (TGA)

Methodology 1

TGA of base vinyl ester and the corresponding nanocomposites is presented in Fig. 15. The incorporation of layered silicate into the vinyl ester matrix increased the thermal stability compared to neat polymer. The TGA curve shows that the nanocomposites exhibited a marginal decomposition temperature at the initial stage which may be traced to the effect of the clay modifiers as well as the Hofmann elimination reaction. It was revealed in the literature that the enhancement of the compatibility between the polymer matrix and the layered silicate can be reached by the addition of an organic modifier such as alkyl-ammonium cation. However, the enhancement in the affinity between the two elements will scarify the thermal stability at initial decomposition temperature due to the degradation of the

alkyl-ammonium cation at an earlier stage which will catalyse the degrading of the polymer [23]. The low clay content of nanocomposites shows higher amounts of onset decomposition temperature. The neat polymer represents 320°C of onset temperature. By the addition of only 0.5 wt.% clay loading, the onset temperature was increased by 4% which represented 331°C. Further additions of layered silicate (i.e. 1 wt.%) enlarged the onset temperature by 6%; at 1.5 wt.% clay loading, the onset temperature reduced to 321°C. In addition, the enlargement of char yield was proportional to the clay content.

As can be seen from Fig. 15, the addition of clay into the vinyl ester matrix has contradicting functions regarding the thermal properties. First, the creation of barrier protection and tortuous path will provide enhancement of the thermal stability. The other one is the catalysing influence of the organic modifier of layered silicate which will decompose the polymer and the thermal properties will be reduced.

The enhancements in thermal properties at low fillers could be attributed to the effect of the barrier properties of layered silicate and the level of dispersion. The intercalation level plays an important role in forming the nanocomposites structure which can help to improve the overall properties. However, the addition of more clay to the polymer matrix could result in reducing the thermal properties due to the catalysing effect that will take place. The results of TGA can confirm the findings of XRD, SEM and TEM.

Methodology 2

Fig. 16 represents the TGA analysis of the neat vinyl ester matrix and corresponding nanocomposites. The addition of layered silicate into the polymer matrix resulted in enhancement of the thermal properties. As can be seen in Fig. 16, all nanocomposites show a slight decomposition at initial temperature as discussed in the previous methodology. The neat polymer shows 329°C, whereas at 1, 2, 3 wt.% clay loading, the onset temperatures were 339°C, 331°C, 332°C respectively. At higher amounts of clay, the onset temperature was slightly reduced. The addition of layered silicate into the polymer matrix has contradicting functions regarding the thermal properties. First, the creation of barrier protection will provide enhancement of the thermal stability. The other one is the catalysing effect of layered silicate which will decompose the polymer and the thermal properties will be reduced. In addition, it was suggested that the lesser amount of clay results in enhancing the thermal properties where the effect of barrier properties will dominate; dispersion should also be achieved. On the other hand, the greater amount of clay led to decrease the thermal stability where the catalysing effect will dominate. The char yield of the nanocomposites was significantly increased which was proportional to the clay content. These findings were in close agreement to the studies by Zhao et al. [24], Gong et al. [25] and Lee et al. [26].
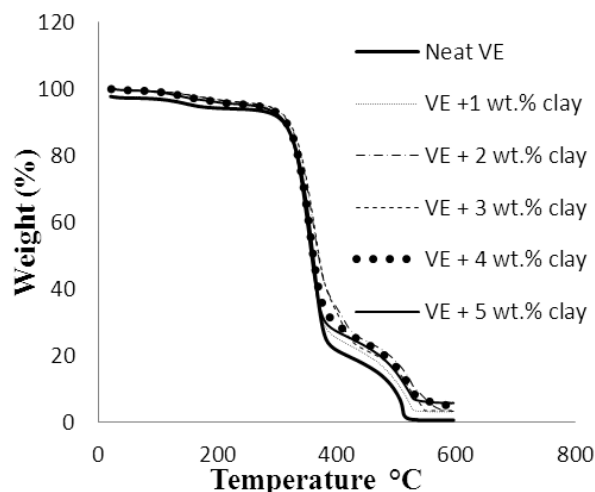
Fig. 16 TGA curve of neat VE and corresponding nanocomposites [5]

2. *Differential Scanning Calorimetry* (*DSC*)

Methodology 1

The study of glass transition temperature of neat vinyl ester and the corresponding nanocomposites was carried out by DSC measurement. Fig. 17 represents the effect of incorporation of layered silicate into the polymer matrix. The neat polymer and the nanocomposites samples almost showed the same T_g, however the addition of layered silicate resulted in decreasing the T_g slightly. The neat polymer represented 142°C and for nanocomposites of 0.5, 1.0, 1.5, 2.0, and 2.5 wt.% showed 140°C, 141°C, 139°C, 140°C and 140°C, respectively. It can be seen that the level of intercalation played an important key for the T_g where 1 wt.% clay loading exhibited the highest amount of T_g compared to the other nanocomposites and as proved by XRD, SEM and TEM that 1 wt.% had the best intercalation level. The reduction of T_g for nanocomposites compared to neat vinyl ester could be attributed to many reasons. First, the level of adhesion between the layered silicate and the polymer matrix can affect the T_g where the lesser amount of adhesion resulted in less tortuous path and barrier properties. Thus, the clay will not restrict the polymer chain mobility. The second reason that affects the T_g could be the formation of interphase (the polymer matrix is closed to the clay surface and the properties are different from the bulk material) in between the layered silicate. The presence of interphase structure can be related to the plasticisation of the polymer surfactants [27]. Moreover, the free volume of the resin can be increased by the addition of layered silicate which has a strong influence on the T_g [28]. In addition, there are many factors that may affect the T_g, such as curing temperature and time [29]-[31], the modification of clay, the level of dispersion and the space between sheets [27].
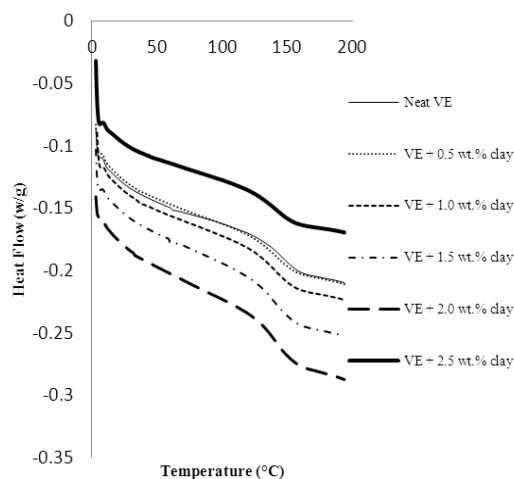

Fig. 17 DSC curve of the neat vinyl ester and the corresponding nanocomposites [4]

Methodology 2

From the DSC results, it was found that the addition of layered silicate into the polymer matrix resulted in a slight decrease in the T_g, however 4 wt.% clay represented almost the same as base polymer. The neat matrix exhibited 143°C and for nanocomposites of 1, 2, 3, 4, 5 wt.% showed 141°C, 141°C, 139°C, 143°C and 142°C, respectively. As proved by XRD, SEM and TEM, the 4 wt.% clay represented a better dispersion level compared to other nanocomposites samples. Thus the T_g of 4 wt.% clay content did not change and it is understood that the level of interaction between the polymer and fillers plays an important factor in the amount of T_g.
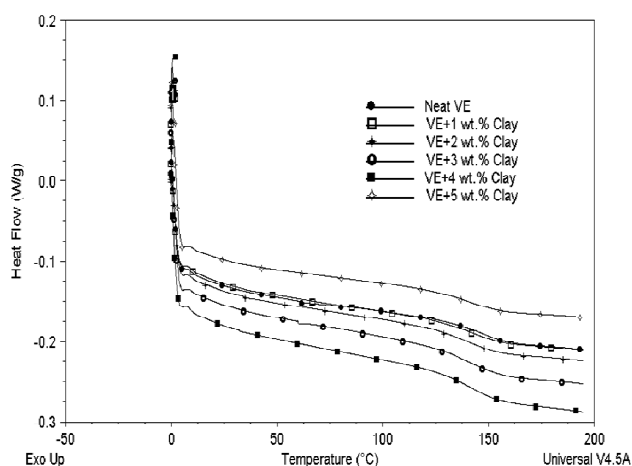

Fig. 18 DSC curve of the neat vinyl ester and the corresponding nanocomposites [5]

Thermal Properties Summary

Table VII summarises the results of onset temperature and glass transition temperature of both methodology 1 and 2. From the table it can be concluded that the processing parameters can have a profound impact on the thermal properties.

TABLE VII
THERMAL PROPERTIES OF METHODOLOGIES 1 AND 2

Methodology	1			2		
Samples	The onset temperature	T_g (°C)	Samples	The onset temperature (°C)	T_g (°C)
VE	320	142	VE	329	143
VE + 0.5 wt.% clay	328	140	VE + 1 wt.% clay	339	141
VE + 1.0 wt.% clay	330	141	VE + 2 wt.% clay	331	141
VE + 1.5 wt.% clay	321	139	VE + 3 wt.% clay	332	139
VE + 2.0 wt.% clay	-	140	VE + 4 wt.% clay	331	143
VE + 2.5 wt.% clay	-	140	VE + 5 wt.% clay	327	142

IV. CONCLUSIONS

The mechanical and thermal properties of neat vinyl ester and the corresponding nanocomposites of two different methodologies were investigated.

Methodology 1 shows that the addition of layered silicate increased the flexural and tensile properties up to 1 wt.% clay loading. The incorporation of more than 1.5 wt.% resulted in decreasing the mechanical properties. The reduction of the nanocomposites properties even at small amounts of clay (i.e. > 1.5 wt.%) could be attributed 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 1 wt.% clay loading. Based on the parameters used in methodology 1, 1 wt.% clay loading was found to be an optimal clay loading. The reason for the optimal clay loading for 1 wt.% is the intercalation level and parameters used as proved by XRD, SEM and TEM compared to other clay loadings in the same methodology.

Further enhancements in the level of intercalation, mechanical and thermal properties were observed in methodology 2. The improvement of mechanical and thermal properties were proportional to the clay content up to 4 wt.% clay loading whereas with methodology 1 it was up to 1 wt.% clay loading.

The flexural modulus and strength of methodology 2 were improved up to 145% and 69% respectively compared to neat polymer whereas methodology 1 showed an improvement up to 64% and 37% of flexural modulus and strength. The tangent modulus of methodology 2 was double that of methodology 1. The improvement of ultimate tensile strength of methodology 2 was almost three times the enhancements in methodology 1.

Methodology 2 was a combination between an upgrade level of processing parameters of methodology 1 and based on different advances thermosetting preparation in the literature [2].

REFERENCES

[1] 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.

[2] 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,* vol. 32, 2013.

[3] S. Lapshin, S. K. Swain, and A. I. Isayev, "Ultrasound aided extrusion process for preparation of polyolefin–clay nanocomposites," *Polymer Engineering & Science,* vol. 48, pp. 1584-1591, 2008.

[4] A. I. Alateyah, H. N. Dhakal, and Z. Y. Zhang, "Mechanical and thermal properties characterisation of vinyl ester matrix nanocomposites based on layered silicate," *World Academy of Science, Engineering and Technology,* vol. 81, pp. 1-8, 2013.

[5] A. I. Alateyah, H. N. Dhakal, and Z. Y. Zhang, "Water absorption behaviour, mechanical and thermal properties of vinyl ester matrix nanocomposites based on layered silicate," *Polymer-Plastics Technology and Engineering,* vol. Accepted, 2013.

[6] C. A. Ittner Mazali and M. I. Felisberti, "Vinyl ester resin modified with silicone-based additives: III. Curing kinetics," vol. 45, pp. 2222-2233, 2009.

[7] I. Southern Clay Products. (11). *Cloisite® 10A.* Available: http://www.scprod.com/product_bulletins/PB%20Cloisite%2010A.pdf

[8] B. S. Institution. (1998). *Glass fibre reinforced plastics — Flexural test —Three point bend method (2746 ed.).* Available: http://www.standardsuk.com/products/BS-EN-2746-1998.php

[9] B. S. Institution. (1998). *Glass fibre reinforced plastics — Tensile test (2747 ed.).* Available: http://www.standardsuk.com/products/BS-EN-2747-1998.php

[10] S. Sinha Ray, K. Yamada, M. Okamoto, and K. Ueda, "New polylactide-layered silicate nanocomposites. 2. Concurrent improvements of material properties, biodegradability and melt rheology," *Polymer,* vol. 44, pp. 857-866, 2003.

[11] J.-H. Chang, Y. U. An, D. Cho, and E. P. Giannelis, "Poly (lactic acid) nanocomposites: comparison of their properties with montmorillonite and synthetic mica (II)," *Polymer,* vol. 44, pp. 3715-3720, 2003.

[12] J. H. Chang and Y. U. An, "Nanocomposites of polyurethane with various organoclays: Thermomechanical properties, morphology, and gas permeability*," *Journal of Polymer Science Part B: Polymer Physics,* vol. 40, pp. 670-677, 2002.

[13] H. Alamri and I. M. Low, "Effect of water absorption on the mechanical properties of nano-filler reinforced epoxy nanocomposites," *Materials & Design,* vol. 42, pp. 214-222, 12// 2012.

[14] H. Alamri and I. M. Low, "Microstructural, mechanical, and thermal characteristics of recycled cellulose fiber-halloysite-epoxy hybrid nanocomposites," *Polymer Composites,* vol. 33, pp. 589-600, 2012.

[15] T. P. Mohan and K. Kanny, "Water barrier properties of nanoclay filled sisal fibre reinforced epoxy composites," *Composites Part A: Applied Science and Manufacturing,* vol. 42, pp. 385-393, 4// 2011.

[16] A. Ashori and A. Nourbakhsh, "Characteristics of wood–fiber plastic composites made of recycled materials," *Waste Management,* vol. 29, pp. 1291-1295, 4// 2009.

[17] M. Avella, A. Buzarovska, M. Errico, G. Gentile, and A. Grozdanov, "Eco-Challenges of Bio-Based Polymer Composites," *Materials,* vol. 2, pp. 911-925, 2009.

[18] P. Jawahar, R. Gnanamoorthy, and M. Balasubramanian, "Tribological behaviour of clay – thermoset polyester nanocomposites," *Wear,* vol. 261, pp. 835-840, 10/20/ 2006.

[19] P. Kodgire, R. Kalgaonkar, S. Hambir, N. Bulakh, and J. P. Jog, "PP/clay nanocomposites: Effect of clay treatment on morphology and dynamic mechanical properties," *Journal of Applied Polymer Science,* vol. 81, pp. 1786-1792, 2001.

[20] S. Pavlidou and C. D. Papaspyrides, "A review on polymer–layered silicate nanocomposites," *Progress in Polymer Science,* vol. 33, pp. 1119–1198, 2008.

[21] M. Alexandre and P. Dubois, "Polymer-layered silicate nanocomposites: preparation, properties and uses of a new class of materials," *Materials Science and Engineering: R: Reports,* vol. 28, pp. 1-63, 2000.

[22] M. L. Q. A. Kaneko, R. B. Romero, R. E. F. de Paiva, M. I. Felisberti, M. C. Gonçalves, and I. V. P. Yoshida, "Improvement of toughness in polypropylene nanocomposite with the addition of organoclay/silicone copolymer masterbatch," *Polymer Composites,* 2013.

[23] P. Kiliaris and C. D. Papaspyrides, "Polymer/layered silicate (clay) nanocomposites: An overview of flame retardancy," *Progress in Polymer Science,* vol. 35, pp. 902-958, 7// 2010.

[24] C. Zhao, H. Qin, F. Gong, M. Feng, S. Zhang, and M. Yang, "Mechanical, thermal and flammability properties of polyethylene/clay nanocomposites," *Polymer Degradation and Stability,* vol. 87, pp. 183-189, 2005.

[25] F. Gong, M. Feng, C. Zhao, S. Zhang, and M. Yang, "Thermal properties of poly(vinyl chloride)/montmorillonite nanocomposites," *Polymer Degradation and Stability,* vol. 84, pp. 289-294, 5// 2004.

[26] W. D. Lee, S. S. Im, H.-M. Lim, and K.-J. Kim, "Preparation and properties of layered double hydroxide/poly(ethylene terephthalate) nanocomposites by direct melt compounding," *Polymer,* vol. 47, pp. 1364-1371, 2/8/ 2006.

[27] A. Yasmin, J. J. Luo, J. L. Abot, and I. M. Daniel, "Mechanical and thermal behavior of clay/epoxy nanocomposites," *Composites Science and technology,* vol. 66, pp. 2415-2422, 2006.

[28] Y.-L. Liu, C.-Y. Hsu, W.-L. Wei, and R.-J. Jeng, "Preparation and thermal properties of epoxy-silica nanocomposites from nanoscale colloidal silica," *Polymer,* vol. 44, pp. 5159-5167, 8// 2003.

[29] T. Lan and T. J. Pinnavaia, "Clay-Reinforced Epoxy Nanocomposites," *Chemistry of Materials,* vol. 6, pp. 2216-2219, 1994.

[30] C. Zilg, R. Mülhaupt, and J. Finter, "Morphology and toughness/stiffness balance of nanocomposites based upon anhydride-cured epoxy resins and layered silicates," *Macromolecular Chemistry and Physics,* vol. 200, pp. 661-670, 1999.

[31] O. Becker, R. Varley, and G. Simon, "Morphology, thermal relaxations and mechanical properties of layered silicate nanocomposites based upon high-functionality epoxy resins," *Polymer,* vol. 43, pp. 4365-4373, 2002.