Mechanical and Thermal Properties Characterisation of Vinyl Ester Matrix Nanocomposites Based On Layered Silicate

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

Abstract—The mechanical properties including flexural 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 and flexural modulus up to 1 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 1 wt.% clay loading, the thermal behaviour 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. Wide Angle X-ray Diffraction, Scanning Electron Microscopy and Transmission Electron Microscopy were utilised in order to characterise the interlamellar structure of nanocomposites.

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

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, thermostet polymers are widely utilised in different applications such as packing, automotive, marina, and insulating materials. However, the use of thermostet in thermal conductivity applications is limited which is attributed to the low thermal conductivity property. Thus, the addition of appropriate fillers such as layered silicate can help to overcome these drawbacks [1]-[3]. 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 properties such as TGA and DSC. 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 special care with the properties such as optical or thermal conductivity, so the addition of Spherical can meet these requirements [4].

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 [4], [5].

In this context, the mechanical (flexural and tensile) and thermal properties (TGA and DSC) 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 thermostet based on layered silicate 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 Fabrication Process

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.

2. 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 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, 0.5, 1, 1.5, 2, and 2.5 wt.%. 

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 40mA and 40kV. 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) 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 30kN load cell. The load was applied midway between the supports. The speed of crosshead was 2mm/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 10mm/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).

Differential Scanning Calorimetry (DSC)

The neat vinyl ester polymer and the corresponding nanocomposites were examined using a TA instrument Q100 DSC. Both the empty reference and the encapsulated pan were inserted inside the DSC device. The specimens were heated and cooled up to 200°C at the rate of 20°C/min. The samples used in this test were in the form of powder extracted from a bulk sample by a knife. The DSC test was made in an inert nitrogen atmosphere.

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 materials 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 microcomposite 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. Table I and Fig. 1 represent the XRD values of neat clay and the corresponding nanocomposites. It can be seen that the addition of layered silicate into the polymer matrix increased the basal distance. The 20 value for only Cloisite 10 A was 20° which indicates 0.443nm 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 0.477nm 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 20 value which was 16.95° and represented 0.523nm of d-spacing. By the addition of 1.5 wt.% layered silicate, the 20 was shifted toward 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, the presence of more clay (i.e. 2.5 wt.%) the 20 was increased and represented 19.98° which was almost as same as the neat clay.

<table>
<thead>
<tr>
<th>TABLE I</th>
<th>XRD RESULTS OBTAINED FROM DIFFERENT CLAY LOADING OF NANOCOMPOSITES</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample No.</td>
<td>20 values at 20°</td>
</tr>
<tr>
<td>Cloisite 10 A</td>
<td>20.00</td>
</tr>
<tr>
<td>VE + 0.5 wt.% clay</td>
<td>18.60</td>
</tr>
<tr>
<td>VE + 1.0 wt.% clay</td>
<td>16.95</td>
</tr>
<tr>
<td>VE + 1.5 wt.% clay</td>
<td>19.20</td>
</tr>
<tr>
<td>VE + 2.0 wt.% clay</td>
<td>19.30</td>
</tr>
<tr>
<td>VE + 2.5 wt.% clay</td>
<td>19.98</td>
</tr>
</tbody>
</table>

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 mixture at high amounts of clay. Thus, agglomeration layers were obtained in the nanocomposites structure.

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, the more the intercalated and partially exfoliated structure. Thus, the improvement in basal spacing led to enhancing the overall properties. In this study the 1 wt.% clay loading exhibited the highest value of d001 spacing. The decreasing in d-spacing of above 1 wt.% layered silicate indicated less interaction which resulted in less improvement of overall properties, as will be discussed in the next section.

2. Scanning Electron Microscopy (SEM)

The SEM images can easily show the level of distribution of the clay through the polymer as seen in Fig. 2. 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. 2 SEM images at 50 µm of (a) 1 wt.% and (b) 2.5 wt.% nanocomposites](image_url)

3. Transmission Electron Microscopy (TEM)

The level of dispersion of 1wt.% and 2.5 wt.% into the
vinyl ester matrix are illustrated in Fig. 3. 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 stack 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.

B. Mechanical Properties

1. Flexural Strength and Modulus

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

Fig. 4 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 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.

Table II

<table>
<thead>
<tr>
<th>Samples</th>
<th>Average maximum Force (N) SD %</th>
<th>Flexural Strength MPa SD %</th>
<th>Improvement in flexural strength %</th>
<th>Flexural modulus GPa SD %</th>
<th>Improvement in flexural modulus %</th>
</tr>
</thead>
<tbody>
<tr>
<td>VE</td>
<td>110.29 +/- 15</td>
<td>52.78 +/- 18</td>
<td>0.00</td>
<td>2.85</td>
<td>0.00</td>
</tr>
<tr>
<td>VE + 0.5 wt.% clay</td>
<td>126.68 +/- 14</td>
<td>58.14 +/- 11</td>
<td>10.14</td>
<td>3.35</td>
<td>17.54</td>
</tr>
<tr>
<td>VE + 1.0 wt.% clay</td>
<td>124.29 +/- 9</td>
<td>72.49 +/- 13</td>
<td>37.33</td>
<td>4.55</td>
<td>59.64</td>
</tr>
<tr>
<td>VE + 1.5 wt.% clay</td>
<td>93.03 +/- 13</td>
<td>69.85 +/- 8</td>
<td>32.34</td>
<td>4.68</td>
<td>64.21</td>
</tr>
<tr>
<td>VE + 2.0 wt.% clay</td>
<td>86.99 +/- 20</td>
<td>49.29 +/- 9</td>
<td>-6.62</td>
<td>4.39</td>
<td>54.03</td>
</tr>
<tr>
<td>VE + 2.5 wt.% clay</td>
<td>61.79 +/- 12</td>
<td>43.83 +/- 3</td>
<td>-16.96</td>
<td>4.20</td>
<td>47.36</td>
</tr>
</tbody>
</table>

Fig. 4 The effect of clay loading on flexural strength

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. 5. The significant improvement in flexural strength and modulus of the 1 wt.% 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 is increased, it can be envisage that the optimal clay loading from 1 wt.% to higher level. As seen in Table II, the clay had a strong influence on the resulting properties where the enhancement in flexural strength and modulus properties were proportional to the clay content up to 1 wt.% clay loading.
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 [10], [11]. 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 [12].

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 [13]-[15].

### 2. Tensile Strength and Modulus

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 III. As seen in Table III, the enhancement of the amount of tangent modulus for nanocomposite samples compared to the pristine one was observed. The clay loading has 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 as same as 1 wt.% and represented 1.29. The addition of more clay led to decreasing the tangent modulus as the examples of 2 wt.% and 2.5 wt.% showed. Fig. 6 illustrates the relationship between the tangent modulus and clay content.

![Graph showing the relationship between tangent modulus and clay content.](image)

**Table III**

<table>
<thead>
<tr>
<th>Samples</th>
<th>Tangent modulus GPa SD</th>
<th>Improvement in Tangent modulus %</th>
<th>Ultimate tensile strength MPa SD</th>
<th>Improvement in UTM strength %</th>
<th>Elongation % SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>VE</td>
<td>1.08 +/- 11 0</td>
<td>13.05</td>
<td>0.00</td>
<td>1.30</td>
<td>+/- 5</td>
</tr>
<tr>
<td>VE + 0.5 wt.% clay</td>
<td>1.15 +/- 14 6.48</td>
<td>16.91</td>
<td>29.57</td>
<td>1.28</td>
<td>+/- 13</td>
</tr>
<tr>
<td>VE + 1.0 wt.% clay</td>
<td>1.30 +/- 10 20.37</td>
<td>19.01</td>
<td>45.67</td>
<td>1.29</td>
<td>+/- 9</td>
</tr>
<tr>
<td>VE + 1.5 wt.% clay</td>
<td>1.29 +/- 11 19.44</td>
<td>18.50</td>
<td>41.76</td>
<td>1.30</td>
<td>+/- 8</td>
</tr>
<tr>
<td>VE + 2.0 wt.% clay</td>
<td>1.29 +/- 4.5 19.44</td>
<td>18.11</td>
<td>38.77</td>
<td>1.01</td>
<td>+/- 14</td>
</tr>
<tr>
<td>VE + 2.5 wt.% clay</td>
<td>1.27 +/- 7 17.59</td>
<td>16.81</td>
<td>28.81</td>
<td>1.04</td>
<td>+/- 6</td>
</tr>
</tbody>
</table>

As can be seen, 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 [13]-[15].

In addition, the elongation is normally decreased with the presence of nanoparticles in polymers which is a sign to measure the ductility of the material [16]-[18]. In this study,
the elongation was marginally reduced compared to the neat polymer.

C. Thermal Properties

1. Thermogravimetric Analysis (TGA) and Derivative Thermogravimetric Analysis (DTG)

TGA and DTG of base vinyl ester and the corresponding nanocomposites are presented in Figs. 8 and 9 respectively. 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 [19]. 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 the Figs. 8 and 9, 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 effect of catalysing that will take place. The results of TGA can confirm the findings of XRD, SEM and TEM. This study is in close agreement to the study by Zhao et al. [20].
The findings of this trend in $T_g$ results were found to be in close agreement to the work carried out by other researchers [21], [26], [27].

2. Differential Scanning Calorimetry (DSC)

The study of glass transition temperature of neat vinyl ester and the corresponding nanocomposites was carried out by DSC measurement. Fig. 10 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 resulted in 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 [21]. Moreover, the free volume of the resin can be increased by the addition of layered silicate which has a strong influence of the $T_g$ [22]. In addition, there are many factors that may affect the $T_g$, such as curing temperature and time [23]-[25], the modification of clay, the level of dispersion and the space between sheets [21]. The findings of this trend in $T_g$ results were found to be in close agreement to the work carried out by other researchers [21], [26], [27].


