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The Effect of Processing Parameters of the Vinyl Ester Matrix Nanocomposites Based On Layered Silicate on the Level of Exfoliation

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***Abstract*—**The study of the effect of the processing parameters on the level of intercalation between the layered silicate and polymer of two different methodology took place. X-ray diffraction, Scanning Electron Microscopy, Energy Dispersive X-ray Spectrometry, and Transmission Electron Microscopy were utilized in order to examine the intercalation level of nanocomposites of both methodologies. It was found that drying the clay prior to mixing with the polymer, mixing time and speed, degassing time, and the curing method had major changes to the level of distribution of the nanocomposites structure. In methodology 1, the presence of aggregation layers was observed at only 2.5 wt.% clay loading whereas in methodology 2 the presence of aggregation layers was found at higher clay loading (i.e. 5 wt.%).

***Keywords*—**Vinyl ester, nanocomposites, layered silicate, characterisations, aggregation layers, intercalation, exfoliation.

I. Introduction

POLYMERS are widely used materials, owing to their advantageous properties such as light weight and ease of manufacturing. However, polymers on their own, certain of their properties are inadequate unless they are modified through addition of fillers and various reinforcements leading to the formation of composite or nanocomposite materials [1]. For that reason and to overcome these drawbacks, suitable fillers (additives) are applied to the neat polymers in order to enhance their properties. Polymers with various particulate fillers have been successfully reinforced to improve their stiffness and toughness, as well as enhancing their resistance to fire and ignition and also their barrier properties. Addition of the particulate fillers often results in unwanted properties such as brittleness and opacity. Also, in these reinforced composites, the dispersion on a nanometre scale between the polymer and the additives is not homogeneous. However, if homogeneous dispersion on a nanometer scale could be reached, the mechanical properties could be further improved and/or new unexpected features might be exhibited [2].

The use of composites and nanocomposites made from inorganic substances of a layered structure like clay has been a subject of elaborate research. However, the subject is experiencing resurgence both in terms of research and industrial activity due to the numerous properties that nanocomposites stand to provide. Several variables associated with materials, that can be controlled, can have a profound influence both on the properties and the structure of the nanocomposite, such as the kind of the clay used, the kind of pre-treatment, the polymer component chosen and the manner in which the nanocomposite incorporates the polymer [2].

Polymer layered silicate nanocomposites have received much attention during the last decade and have great interest both in the academic field and in industry [3], [4], since they often give more attractive improvement to material properties than both micro and macro composite materials [5]-[9]. The improvement can be mechanical (high strength, modulus, and flexural) or thermal (thermal gravity analysis).They also exhibit different properties such as decreased gas permeability and flammability [9], [10], increased biodegradability and barrier properties [8]. These materials are reported to be 21st century materials as their unique properties and design are not found in traditional composites [2].

Relying on the strength of the interaction between the polymers and layered silicates (which are treated or not), three varied phases of nanocomposites are thermodynamically obtainable. First of all there are intercalated nanocomposite structures; this phase occurs when one or more lengthened polymer chains is intercalated within the layered silicate. The effect of that is a well-organized multilayer structure with reciprocally acting polymeric and layered silicate layers. The dispersion between the platelets normally is between 20-30 Å. Secondly, flocculated structures nanocomposites, which are similar to the previous stage in conception, but the difference is in the position of layered silicates since normally they are flocculated. Finally, exfoliated or delaminated structures nanocomposites. Usually, this phase is achieved when the concentrations of the layered silicates are significantly lower than in the intercalation system. The exfoliation occurs when layered silicate layers are dispersed in a continuous polymer matrix via median distance, which is dependent on the clay content [9]. In other words, exfoliated or delaminated structures are produced when the layered silicate layers are effectively separated from one another and separately incorporated in the repeated polymer matrix [11]-[14]. The separation between the platelets in the exfoliation stage is between 80-100 Å [2].

In this context, the study of the influence of the processing

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parameters on the level of intercalation took place. Two earlier works [15] and [16] showed that the level of intercalation and the affinity between the polymer and the layered silicate really depend on the processing parameters.

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" [17]. 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 [18].

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 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 ($\lambda = 1.542$A) 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. Energy Dispersive X-ray Spectrometry (EDS)

The morphology of the VE / nanocomposite structure was further examined using a Jeol JSM 6060LV microscope working at an operating voltage of 8 kV. The degree of dispersion between the layered silicate and the vinyl ester matrix of the nanocomposites samples was measured using Energy Dispersive Spectroscopy (EDS), a by-product of the back-scattered electrons off the specimen from the electron beam. The principle of this method is that when electrons are directed at the sample, characteristic X-rays are emitted for all atoms with an atomic number above that of Na. This enables an elemental distribution map to be created for any element with $Z > Na$; in this case the Al and Si found in the layered silicate and the Cl from the vinyl ester.

4. 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.

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 exhibit 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 0.523 nm 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.

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 [15].

TABLE I
XRD Results Obtained from Different Clay Loading of Nanocomposites of Methodology 1 [15]

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

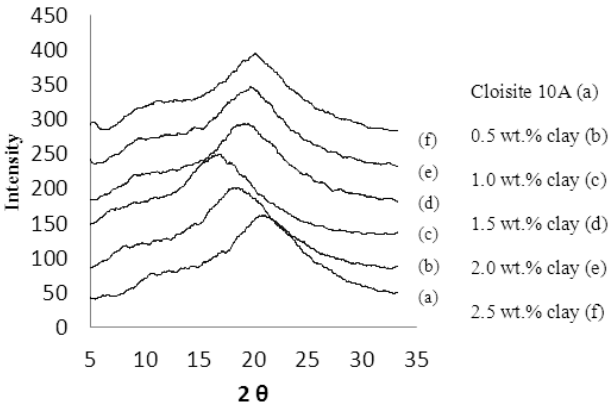

Fig. 1 XRD curve of Cloisite 10A and the corresponding nanocomposites of methodology 1[15]

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 of 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 of 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 0.551nm 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 the high viscosity mixture at high amounts of clay [16].

TABLE II
XRD RESULTS OBTAINED FROM DIFFERENT CLAY LOADING OF NANOCOMPOSITES OF METHODOLOGY 2 [16]

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

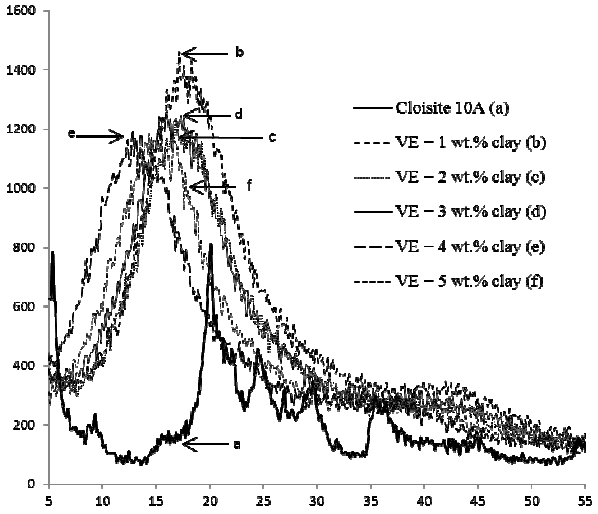

Fig. 2 XRD curve of Cloisite 10A and the corresponding nanocomposites of methodology 2 [16]

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 distances, 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 [19]-[21]. 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 [15], 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.

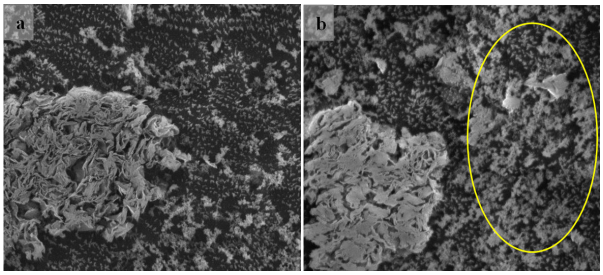

Fig. 3 SEM images at 50μm of (a) 1 wt.% and (b) 2.5 wt.% nanocomposites [15]

Methodology 2

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.

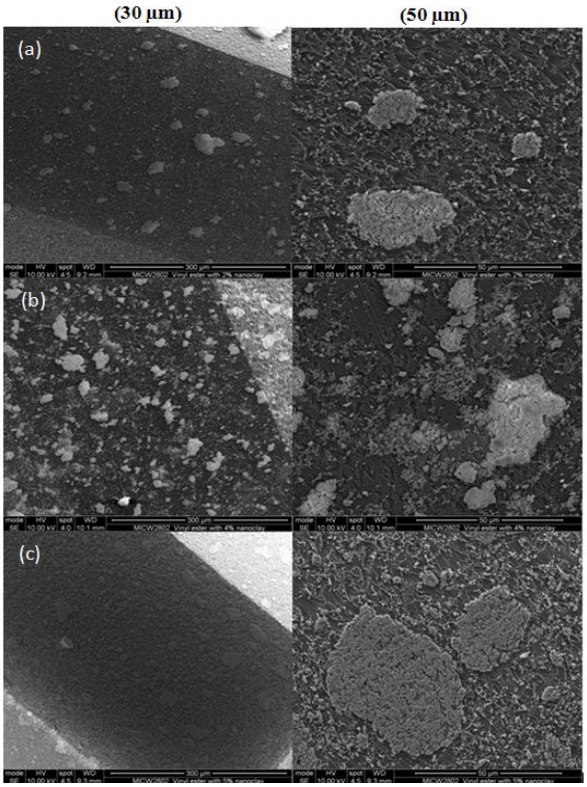

Fig. 4 SEM images at 30 µm and 50 µm of (a) 2 wt.%, (b) 4 wt.% and (c) 5 wt.% nanocomposites [16]

3. Energy Dispersive X-ray Spectrometry (EDS)

Methodology 1

Fig. 5 represents the dispersion of different amounts of clay into the vinyl ester matrix. It was found that the incorporation of the layered silicate into the polymer matrix was fairly homogeneous with a little bit of agglomerative layers at higher clay loading levels. In addition, it was found that the increasing of the clay concentrations led to enlarging the clay agglomeration as the viscosity was increased. The layered silicate in Fig. 5 can be seen as white points which reflected the Si element. The uniformity of intercalation was observed at small clay loading such as 1 wt.%. The addition of only 1.5 wt.% clay resulted in building the aggregation layers as the viscosity was increased. Further incorporation of clay such as 2 wt.% led to dramatic increasing in the agglomerative level. The lack of distribution between the polymer and layered silicate could be related to the processing parameters which include drying the clay prior to the mixing with the polymer, the mixing time and speed, and the degassing time. As the viscosity is increased the improvement of processing parameters is needed.

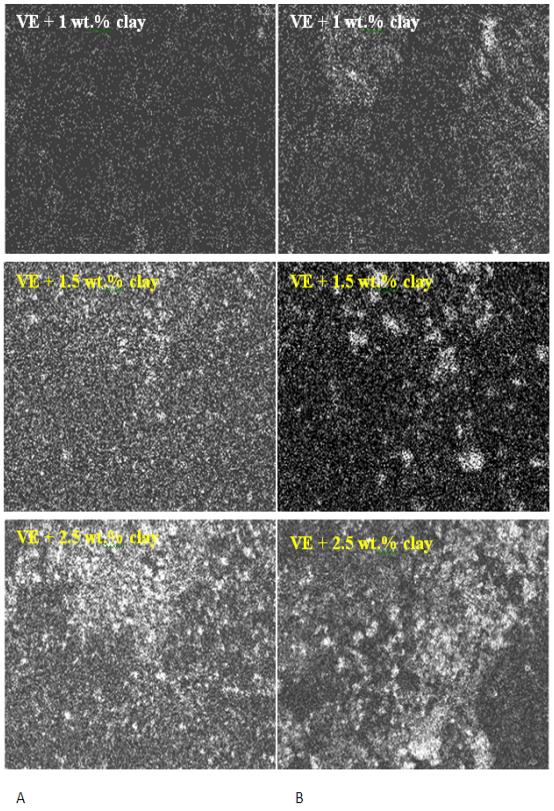

Fig. 5 EDS images at different magnification (a) (55X) and (b) (500X) of 1 wt.%, 1.5 wt.% and 2.5 wt.% nanocomposites

Methodology 2

The EDS images of the second methodology are presented in Fig. 6. It was found that the incorporation of the layered silicate into the polymer matrix was fairly homogeneous with a little bit of agglomerative layers at higher clay loading level. In addition, it was found that the increasing of the clay concentrations led to enlarging the clay agglomeration as the viscosity was increased. At 2 wt.% clay loading, the dispersion of clay into the polymer matrix was uniform and no agglomeration layers were observed at different magnifications of EDS. By the addition of more clay (i.e. 4 wt.%), the nanocomposites structure exhibited good intercalation although the aggregation of a few layers was obtained. As seen in Fig. 6 (a), the aggregation of layered silicate appeared in one side of the sample which was attributed to the insufficient mixing process as the viscosity was increased. In addition, the incorporation of high amounts of clay, such as 5 wt.%, led to decreasing the homogeneity and enlarging the aggregation and the micro-voids in the nanocomposites structure as seen in Fig. 3. The black circles on the EDS image represent the high amount of agglomeration layers at high amount of clay loading (i.e. 5 wt.%). This explains the reduction in the d-spacing value as was calculated by XRD and confirms the results by SEM.

Energy Dispersive X-ray Spectrometry Summary

In the comparison between the two methodologies, it can be

seen that the processing parameters are the key to achieving a good intercalative level between the polymer and the layered silicate. In methodology 1, such as 2.5 wt.%, the good distribution was not reached and the existence of aggregation layers took place, whereas in methodology 2 and at almost the double amount of clay (i.e. 4 wt.%) a uniform distribution was observed. As a result, appropriate processing parameters must be followed in order to achieve remarkable progress in the level of intercalation of nanocomposites.

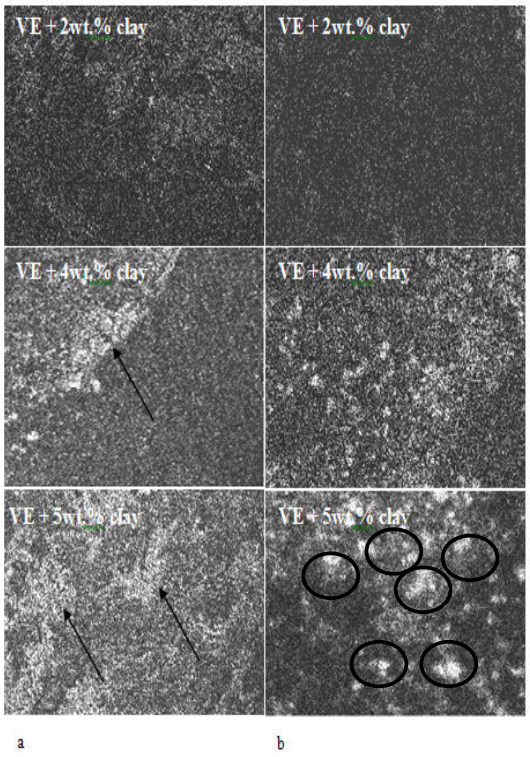

Fig. 6 EDS images at different magnification (a) (55X) and (b) (500X) of 2 wt.%, 4 wt.% and 5 wt.% nanocomposites [16]

4. Transmission Electron Microscopy (TEM)

Methodology 1

Our previous work on the methodology 1[15] showed that the level of dispersion of 1wt.% and 2.5 wt.% into the vinyl ester matrix are illustrated in Fig. 7. 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, EDS, and SEM findings.

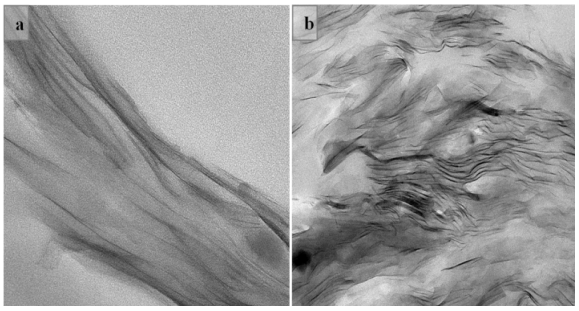

Fig. 7 TEM micrographs at 50 nm magnification of (a) 1 wt.% and (b) 2.5 wt.% nanocomposites [15]

Methodology 2

Fig. 8 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 amounts 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 the amount of clay loading mixed with the polymer, the less exfoliated and aggregated the nanocomposites structure [2]. These findings support the results by XRD, SEM and EDS [16].

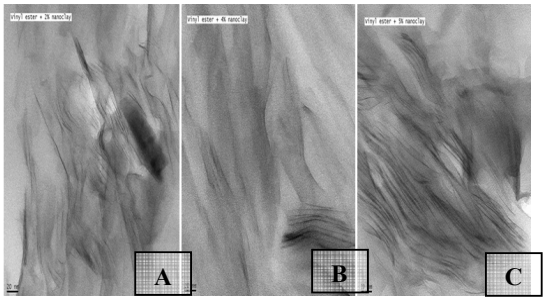

Fig. 8 TEM micrographs at 20 nm magnification of (a) 2 wt.%, (b) 4 wt.% and (c) 5 wt.% nanocomposites [16]

IV. Conclusions

The outcomes of different structures, whether they form a nanocomposite or not, rely upon many factors. The polymer, clay source and modification, and the type of preparation, are all factors that have an influence.

The processing parameters had a profound impact on the resulted structure of nanocomposites as seen in the characterisations of methodology 1 and 2. X-ray diffraction, Scanning Electron Microscopy, Energy Dispersive X-ray Spectrometry, and Transmission Electron Microscopy were used to prove that the level of intercalation of nanocomposites depends on the preparation method and parameters used.

Methodology 1 showed a limited enhancement in the enlarging of the layered silicate basal distance, where the improvements of clay distance was up to 1 wt.% clay loading. However, methodology 2 represented remarkable improvements of the level of intercalation nanocomposites as the partially exfoliated nanocomposites system was reached at 4 wt.% clay loading.

The study of the level of intercalation between the layered silicate and polymer is important as the well-dispersed nanocomposites structure will provide more enhancements in different properties.

With regard to the improvement of properties, most of the exfoliation structure of nanocomposites gains by enhanced strength and modulus. Also, the barrier properties, storage of modulus, thermal stability and flame retardance have been improved, according to many reports. By contrast, there are concerns regarding some properties such as elongation and toughness. In addition, some properties were improved more by the intercalation structure compared to exfoliation nanocomposites, such as toughening and impact. The aggregation of layered silicate imparted side effects of the resulting properties such as in flame retardance where the aggregation layers acted as a source of heating.

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