Contact Angle Measurement of the Vinyl Ester Matrix Nanocomposites Based On Layered Silicate

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

Abstract—Contact angle measurement was utilized in order to study the subject of the wettability and surface chemistry of the nanocomposites materials. Water and glycerol droplets were used in this study. The incorporation of layered silicate into the vinyl ester matrix helped to improve the wettability and reduced the θ values of both liquids used. The addition of 2 wt.% clay loading reduced the θ values of water and glycerol by up to 21% and 6% respectively. Likewise, the incorporation of 4 wt.% clay loading reduced the water and glycerol θ values by 49% and 38% respectively. Also this study confirms the findings in the literature regarding the relationship between the intercalation nanocomposites level and the wettability. 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, characterisations, contact angle measurement, wettability.

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 nanometer 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 intraditional composites[2].

The nanocomposites usually exhibit a very high amount of barrier properties with even a small amount of layered silicate [11]. Tortuous paths help to understand the principle of the barrier behaviour and its enhancement in the nanocomposites. This action can be explained by the introduction of the impermeability of the layered silicate into the matrix of polymer, so the intercalation molecules are placed in a wiggle shape around the nanoparticles in a random way [2], [9], [12]-[14]. Because of the ratio of large length to width of the sheets, this type of clay will enhance the path length when compared to different nanoparticles geometry [9], [15], [16].

In order to study the subject of the wettability and chemistry surface of the nanocomposites materials, the contact angle measurement is widely used and has an empirical indication. This method determines the solid-liquid-vapour system by using Young's equation [17], [18]. The studying of the chemistry surface of nanocomposites is very important as is the understanding of the wetting behavior in relation with the nanocomposites performance.

In this context, the study of the wettability of the neat vinyl ester and the nanocomposites samples took place. Also, the study of the relationship between the level of nanocomposites intercalation and the wettability is presented.

II. EXPERIMENTAL

A. Materials

The matrix material used in this study is vinyl ester (VE) resin. "Vinyl ester resins are oligomers resulting from the

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reaction between bisphenol-A based epoxy oligomers and unsaturated carboxylic acids, such as acrylic or methacrylic acid, which provide unsaturated terminal sites" [22]. 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 [23].

B. Sample Fabrications Process

1) Methodology

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. Characterization

1) Wide Angle X-ray Diffraction (WAXD)

WAXD analysis on compression-moulded specimens was used to determine the clay intercalation and interlayer spacing utilizing a Philips APD 1700 X-ray diffraction system with Cu Kα radiation (λ = 1.542A) generated at 40mA 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.

D. Contact Angle Measurement

Contact angle measurements were utilised in order to assess the affinity of the samples used (neat and nanocomposites) with the plasticizers (water and gylcerol). 3 μl volume drops of MilliQ grade water and glycerol were deposited on the surface ofneat and corresponding nanocomposites samples with a syringe. Pictures of the drops were acquired through a digital camera positioned on a static contact angle analyzer. The θ of the contact angle was measured automatically from the image setup. The image of the solvent droplet can determine the diameter, D, and the height, h, and the following equation was utilised in order to find out the contact angle of different surfaces.

$$\tan\left(\frac{\theta}{2}\right) = \frac{2h}{D} \qquad (11)$$

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-

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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.

From Table I and Fig. 1, 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. 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. 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 0.640 nm. 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 [24].

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 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 [25]-[27]. Thus, the methodology which was followed was in close agreement to the findings of the literature.

2) Scanning Electron Microscopy (SEM)

The SEM examination in Fig. 2 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.

TABLE I
XRD RESULTS OBTAINED FROM DIFFERENT CLAY LOADING OF NANOCOMPOSITES OF METHODOLOGY 2[24]

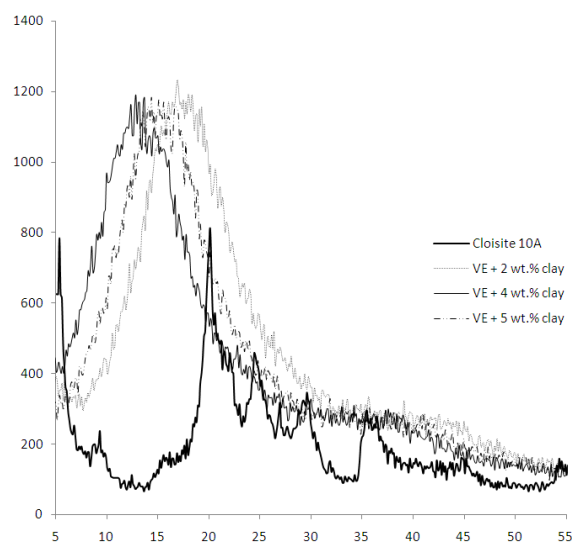| Sample No.	2θ values at 20°	The interlayer distances (nm)	d-spacing improvement %
Cloisite 10 A	20.00	0.443	00.00
VE + 2 wt.% clay	16.86	0.525	18.51
VE + 4 wt.% clay	13.84	0.639	44.24
VE + 5 wt.% clay	16.08	0.551	24.38

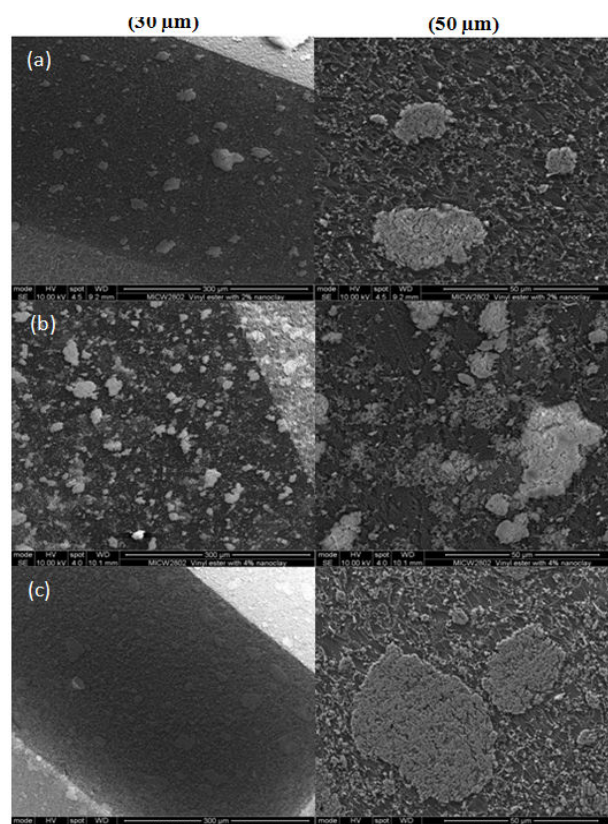Fig. 1 XRD curve of Cloisite 10A and the corresponding nanocomposites of methodology 2 [24]

Fig. 2 SEM images at 30 μm and 50 μm of (a) 2 wt.%, (b) 4 wt.% and (c) 5 wt.% nanocomposites[24]

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3) Energy Dispersive X-ray Spectrometry (EDS)

The EDS images of the second methodology are presented in Fig. 3. 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. 3 (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. 2. 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.
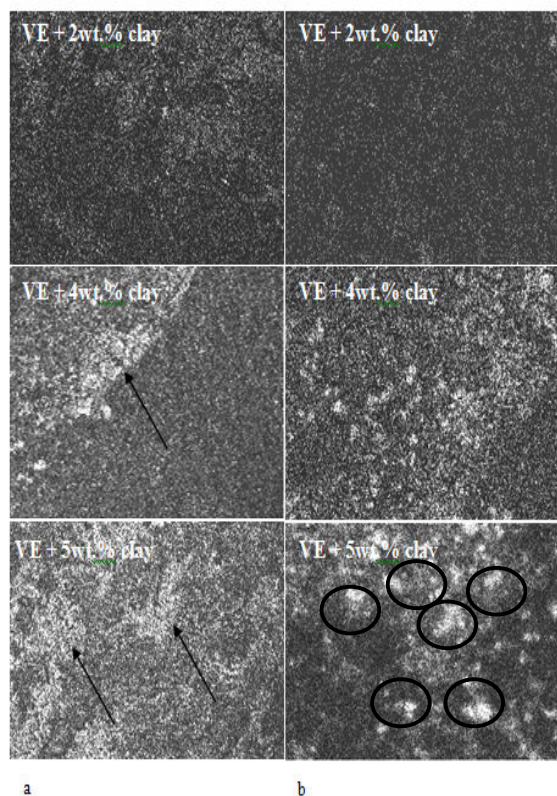

Fig. 3 EDS images at different magnification (a) (55X) and (b) (500X) of 2 wt.%, 4 wt.% and 5 wt.% nanocomposites[24]

4) Transmission Electron Microscopy (TEM)

Fig. 4 shows the TEM micrographs of 2, 4, and 5 wt.% nanocomposites samples at higher magnification (20nm),

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. 4. 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[24].
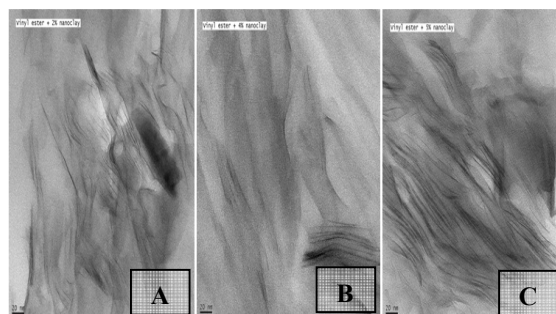

Fig. 4 TEM micrographs at 20 nm magnification of (a) 2 wt.%, (b) 4 wt.% and (c) 5 wt.% nanocomposites [24]

B. Contact Angle Measurement

In order to study the subject of the wettability and chemistry surface of the nanocomposites materials, the contact angle measurement is widely used and has an empirical indication. This method determines the solid-liquid-vapour system by using Young's equation [17], [18]. The studying of the chemistry surface of nanocomposites is very important as is the understanding of the wetting behaviour in relation with the nanocomposites performance. Also, to achieve more advanced and desirable nanocomposites applications [9], [18]-[20]. The wettability can also describe the progress of the intercalation between the polymer and layered silicate as the clay galleries depend on the wetting at the melt/solid interaction [21].

The results of the contact angle measurement according to the experiment procedures mentioned in the experimental part for the average of four samples are illustrated in Table II.

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TABLE II
CONTACT ANGLE VALUES OF NEAT VINYL ESTER AND THE CORRESPONDING
NANOCOMPOSITESOF BOTH WATER AND GLYCEROL

Sample	water droplet (θ)	glycerol droplet (θ)
Neat vinyl ester	91.76	96.7
Vinyl ester + 2 wt.% clay loading	75.58	90.5
Vinyl ester + 4 wt% clay loading	61.67	70.1

The θ values of both liquids showed that the neat polymer represented more hydrophobicity behaviour which means less wettability property. The affinity of the solvent droplet to the sample surface was proportional to the clay content as seen in Fig. 5. By the addition of layered silicate into the polymer matrix, the angle of both liquids was decreased. At 2 wt.% clay loading, the θ values of water and glycerol were decreased by 21% and 7% respectively compared to the neat polymer.

At 4 wt.% clay loading, the contact angle values were decreased sharply by up to 49% and 38% of glycerol and water droplets respectively compared to pristine polymer.

It was found in the literature that the contact angle measurement can also provide the level of intercalation between the layered silicate and the polymer [2]. Thus, the decreasing of the θ values were proportional to the clay content which indicated the enhancement in the level of nanocomposites intercalation which can be correlated to the characterisation techniques that were mentioned above.

Fig. 5 Contact angle of solvents (glycerol and water) droplet of neat, 2 wt.% and 4 wt.% nanocomposites

XRD, SEM, EDS, and TEM show that the good intercalation level was proportional to the clay content up to 4 wt.% clay loading. As a result, contact angle measurement has proved the results by these characterisations and also proved the findings in the literature regarding the relationship between the contact angle measurement and the level of intercalation.

IV. CONCLUSIONS

XRD, SEM, EDS, and TEM characterisations results showed that the addition of layered silicate into the polymer matrix successfully formed intercalated and partially exfoliated nanocomposites.

This study confirmed that using contact angle measurement for studying the wettability subject of the nanocomposites is a useful and reliable technique as well as measuring the level of intercalation which can act as a low cost device.

The presence of the layered silicate into the polymer matrix can increase the wettability of the samples. The ultimate enhancement in the wettability in this study was found at 4 wt.% clay loading.

In addition this study supports the findings in the literature regarding the relationship between the level of intercalation of nanocomposites and wettability.

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