A STUDY OF CLAY-EPOXY NANOCOMPOSITES CONSISTING OF UNMODIFIED CLAY AND ORGANO CLAY

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Abstract

Clay-epoxy nanocomposites were synthesized from DGEBA resin and montmorillonite clay with an in-situ polymerization. One type of untreated clay and two types of organo clay were used to produce the nanocompsoites. The aims of this study were to examine the nanocomposite structure using different tools and to compare the results between the unmodified clay and modified clays as nanofillers. Although diffractogram in reflection mode did not show any apparent peak of both types of materials, the transmitted XRD (X-Ray Difraction) graphs, DSC (Differential Scanning Calorimeter) analysis and TEM (Transmission Electron Microscope) images revealed that the modified clay-epoxy and unmodified clay-epoxy provides different results. Interestingly, the micrographs showed that some of the modified clay layers possessed non-exfoliated layers in the modified clay-epoxy nanocomposites. Clay aggregates and a hackle pattern were found from E-SEM images for both types of nanocomposite materials. It is shown that different tools should be used to determine the nanocomposite structure.

Keywords: epoxy resin, montmorillonite, XRD, DSC

1. Introduction

Polymer layered silicate nanocomposites (PLSNs) have emerged among the other nanomaterials for over the past decade. Layered silicates, with their high surface area and aspect ratio, give a high reinforcement efficiency even at low contents (1–5%). Conventional composites usually use high loadings of micro fillers (30 – 50%). So that, PLSNs are promising materials in the future as the need of layered silicates is low and the price of layered silicates is reasonably cheap. More over, silicate addition enhances mechanical properties, optical properties, gas barrier properties and, heat distortion temperature [1-4].

Montmorillonite or MMT, one of the common silicates, is a crystalline, 2:1 layered clay mineral in which a central alumina octahedral layer is sandwiched between two silica tetrahedral layers [5]. The layers are separated by a regular spacing, which is commonly termed as gallery. Thus, the layers themselves are in negative charges, and they are usually balanced with $Mn^+.xH_2O$ (typically Ca^{2+} / Mg^{2+} or Na^{2+} /K^{2+}) are located naturally on the MMT layers. This results in that MMTs possess hydrophilic property and are not able to react with any polymer. However, MMTs have the ability to exchange ions, which means the clay layers are modified by an onium ion substitution reaction. Alkylammonium cations provide functional groups so that the clay then becomes possible to react with organics. In other words, without cation exchange reaction, the monomer or polymer is not able to move into the clay gallery.

A number of different groups have worked on clay-epoxy systems [6]. The basic principle of PLSN synthesis is that the polymer or its monomer is able to move in and react within the inter layer galleries of the layered silicate. The molecules will intercalate into the gallery when the nature and polarity of the layered silicate gallery is similar to that of the resin and the hardener. A thermodynamic equilibrium between the surface energy of the layered silicate and the polarity of the

swelling monomers determines the intercalation process. The curing process in the galleries changes this equilibrium and enables further reactive monomers to diffuse into the gallery. This dispersion process results in the increase of the gallery distance. Then, a balance between the intergallery and extragallery polymerization rate is critical to achieve intercalation and subsequent exfoliation [7]. The kinetic study of this material is usually examined by DSC. Only one exothermal peak is observed by DSC [8-14]. The addition of organo silicates shifts the exothermal peak to lower temperature [8, 9, 10, 11]. This suggests that the surface of the modified clay plays a significant role in the homopolymerization. More over, Chin believed that 40% of a total ΔH was used in an exfoliation process [9].

The establishment of PLSN structure is quite complicated and influenced by a significant number of factors, such as the nature of the clay and the polymer, the processing parameters, and the clay layer distribution, which relates to the heterogeneity. When the clays are dispersed in the polymer, two types of PLSN structures can be obtained, namely intercalated and exfoliated structures. When a small increase of the gallery distance occurs, intercalated structures are formed. On the other hand, when the silicate layers are well separated and individually dispersed in the polymer matrix, exfoliated structures are formed. Since the latter structure is more homogeneous than the former, exfoliated nanocomposites exhibit better properties. However, it is difficult to obtain an exfoliated structure by itself. In fact some studies show that polymer nanocomposites possess mixed structures or an intercalated structure only [10]. XRD and TEM are a common practice to determine the PLSN structure. AFM (Atomic Force Microscopy) is another tool to observe the morphology of the surface. However, a more precise study should be conducted to quantitatively determine the nanocomposite structure.

The majority of the work on the clay-epoxy systems has focused on the synthesis and characterization of physical and some mechanical properties. In this work the kinetic study of the unmodified clay-epoxy and organo clay-epoxy as well as the clay-epoxy-hardener mixtures was examined using DSC. The morphology of the materials was observed using TEM and reflected XRD methods. To support the XRD in the reflection mode, a transmitted XRD method was also applied. The objectives of this research were to investigate the influence of organo clay and unmodified clay to the morphology of the clay-epoxy systems using different tools.

2. Experimental

The material used in the present work was Diglycidyl ether of bisphenol A / DGEBA resin (Araldite Algy 9708-1) purchased from Ciba-Geigy combined with 1-Methylimidazole (1-MI), purchased from Aldrich, as the curing agent. The fillers were commercial MMTs, namely Nanomer I30E, Cloisite 30B and Cloisite NA$^+$. Here after, the fillers are identified as I30E, C30B and CNA.

The epoxy and clay powder were dried overnight at 50 °C in a vacuum prior to sample production. Unfilled epoxy specimens were made by mixing the epoxy resin and 2.5 wt% hardener and then blending them in a SpeedMixer at 3000 rpm for 1 min. Filled specimens were synthesized by mixing the desired amount of clay with epoxy resin at (76 ± 1)°C using an overhead stirrer for 30 min; 2.5 wt% of hardener was then added into the mixture and mixed in the SpeedMixer at 3000 rpm for 1 min. The blend was poured into release-agent-coated-aluminum moulds with mylar-sheet-covered glass bases, then cured at 160 °C for 2 hours, and followed by a post-cure at 180 °C for 2 hours.

Circular moulds with a diameter of 25 mm and a thickness of 2 mm were prepared. The coin-shaped samples were ground using sand paper of 1200 grid to obtain a homogenous thickness of 1mm. These samples were used for XRD observations.

Differential Scanning Calorimeter (DSC) analyses were conducted on a Perkin-Elmer DSC-7 using Pyris software. Calibration was carried out prior to measurements using indium and zinc standards. Liquid samples of 15-25 mg weight were sealed in aluminum pans and heated from 25 °C – 400 °C at a scanning rate of 10 °C/min.

X-ray diffraction (XRD) analysis was performed using a Phillips PW 1130 generator which was equipped with Traces software. A voltage of 40kV and current of 25mA were employed for Cu Kα radiation. Measurements were performed in a range of $2\theta = 1° – 30°$ for the unfilled and filled epoxy samples as well as the dried MMT powder. The reflected and transmitted methods were applied for all samples.

Transmission Electron Microscope (TEM) samples were cut using a Leica Reichert Ultracut S Microtome with a Diatome diamond knife, which was placed at an angle of 6°. The 70 nm thickness of sections were collected on

hexagonal 300 mesh copper grids. The images were obtained from a Phillips EM 420 Transmission Electron Microscope (TEM), which was operated in bright field mode at 100 kV.

3. Results and Discussion

MMT epoxy based nanocomposites were synthesized by in-situ polymerisation. Six MMT-epoxy systems were produced from the three organoclays and two different clay loadings 2.5wt% and 5wt%.

DSC studies of MMT-DGEBA for the I30-DGEBA, C30B-DGEBA and CNA–DGEBA systems are shown in Figure 1a. Only one exothermal peak is observed for the I30E-DGEBA and C30B-DGEBA systems and it is obvious that the untreated CNA clay does not swell in the DGEBA. These thermograms demonstrate that a reaction between clay and the epoxy takes place at a temperature range of 212 – 221 °C for the I30E- DGEBA systems and of 289 – 296 °C for the C30B-DGEBA systems. These two thermograms show a contrast result. For the I30E-DGEBA systems, the peaks shift towards lower temperature due to enhanced reaction rate with the increasing clay content. In contrast for the C30B-DGEBA systems, the peaks shift toward higher temperature due to inhibited reaction rate with the increasing clay content.
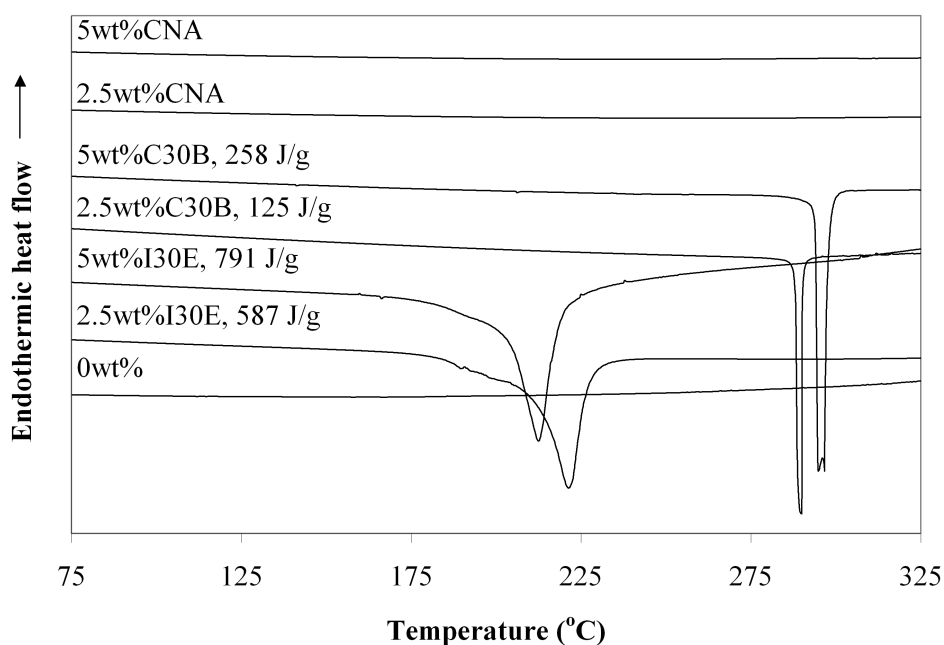

Figure 1(a). DSC analysis of DGEBA and MMT-DGEBA, showing the swelling process in the I30E-DGEBA and the C30B-DGEBA systems
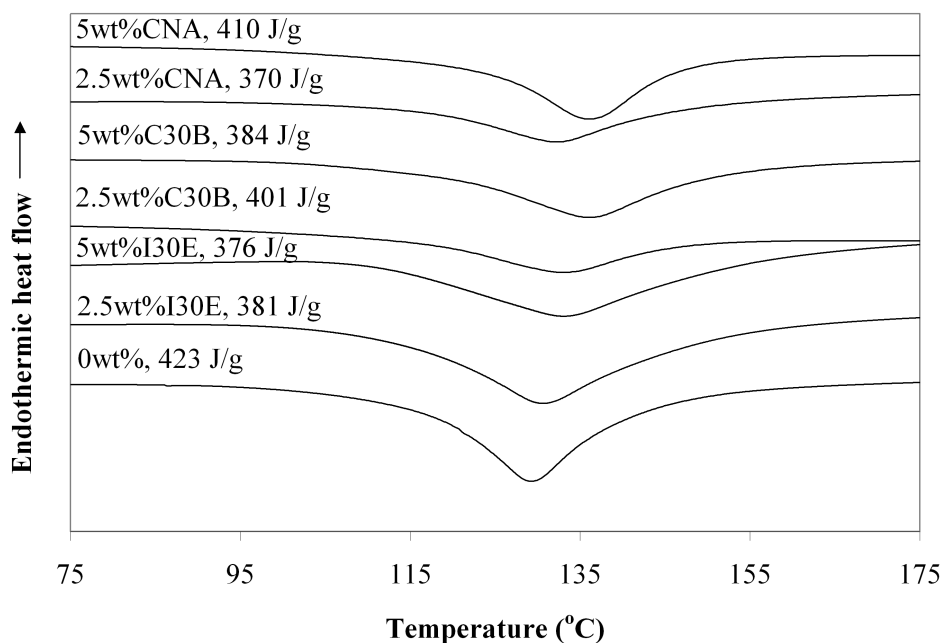
Figure 1(b). DSC analysis of curing agent-DGEBA and MMT-curing agent-DGEBA

These results suggest that the I30E organoclay play a catalytic role in the homopolymerization of DGEBA [8]. The DSC results also show that the heat released by the systems increases as the clay content increases. This also indicates that a spontaneous clay-DGEBA reaction process takes place at the above temperature range.

Figure 1b shows the DSC results of the MMT- hardener-DGEBA- mixtures of the I30- hardener-DGEBA, C30B-hardener-DGEBA, and CNA– hardener-DGEBA systems. Similar to previous studies, one exothermal peak is observed in the thermograms. The epoxy polymerisation takes place in the onset temperature of 129 °C and the heat released is 423 J/g. These thermograms demonstrate that a reaction occurred in the mixtures at a temperature range of 131 – 136 °C for all systems. This indicates that the presence of MMT, both modified and unmodified, does not impede greatly the reaction between the epoxy and the curing agent, even though the onset temperature obtained is slightly higher than that of the unfilled epoxy. Some amount of heat is consumed for the reaction between the MMT and the epoxy as the heat released of the MMT-epoxy systems are lower than that of the epoxy. This result is in accordance with previous studies [9, 11]

Comparing Figures 1a and 1b, it is obvious that curing agent addition shifts the exothermal peak to a lower temperature for the I30E-epoxy and C30B-epoxy cases. The explanation for this is that the viscosity became high during the curing process of epoxy, which means the three-dimensional cross-linking process occurred. So that, the reaction takes place in the temperature range of 131 – 136 °C, near the epoxy polymerisation temperature, instead of in the temperature above 221 °C. A few previous studies also showed similar results with the current result [9, 11, 14]. In this critical state, a balance between the intergallery and extragallery polymerization rate determined the opening of the gallery layers.

The heat released, as shown in Figures 1a and 1b, are in contrast for the I30E-epoxy and C30B-epoxy systems. The heat released by the I30E-DGEBA is bigger and by C30B-DGEBA is smaller than by their nanocomposite systems. This indicates, once again, that the I30E plays a catalytic role while the C30B plays an incatalytic role. This relates with their active exchanged ions on their clay surfaces. The exchanged ion is, in fact, one of the key factors in intergallery and extragallery polymerization rate, and at the end this determines final gallery distance.

Figure 2 is powder diffractograms of pure dry MMT for the three different organoclays. They show a strong peak due to (001) corresponding to a d-spacing of   2.2 nm, 1.83 nm, and 1.21 nm for I30E, C30B and CNA organoclays respectively. Moreover, the (002) and (101) peaks are quite evident for I30E and C30B organoclays.

Figure 3a and 3b shows the reflected and transmitted XRD patterns of nanocomposites respectively. The clay (001) peak is not apparent in the reflected patterns for
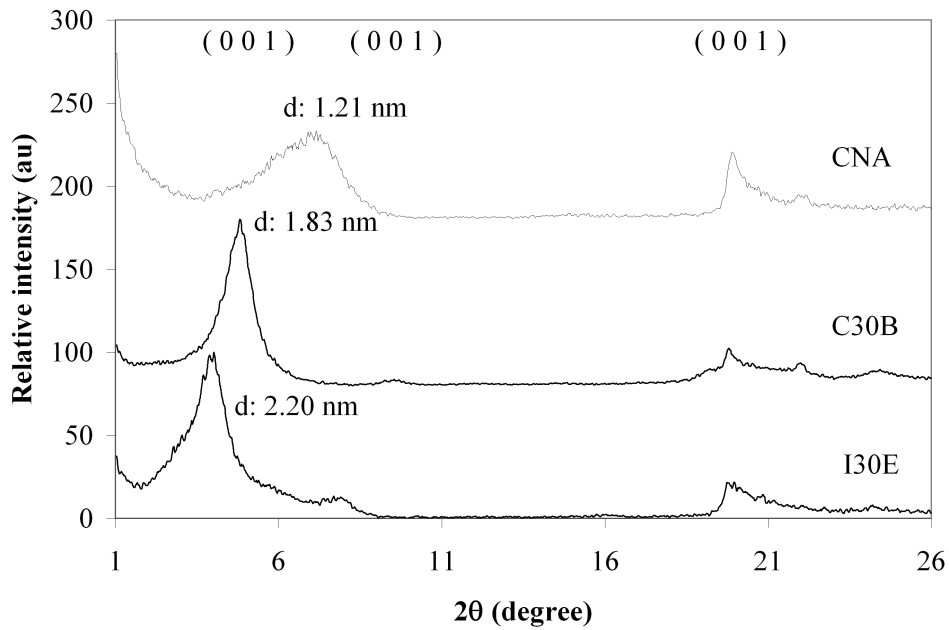

Figure 2. XRD patterns of dry MMTs.

all systems and a broad peak at $2\theta = 17.5°$ appeared in these patterns. This broad peak shows the epoxy was in an amorphous state. In general, the reflected XRD pattern is a typical diffractogram of nanocomposites and this indicates that the d-spacing of clay galleries expanded up to a bigger d-spacing value than 8.8 nm ($2\theta = 1$). It is interesting to note that the (001) peak of CNA also disappeared, which suggested that CNA organoclay layers were exfoliated. From the transmitted XRD analysis, two broad peaks of the amorphous unfilled epoxy can be seen in Figure 3b. It is obvious for the I30E-epoxy and C30B-epoxy systems that the higher the clay contents, the flatter the peaks. These patterns verify that the organoclay particles were well dispersed in the epoxy, forming more amorphous states
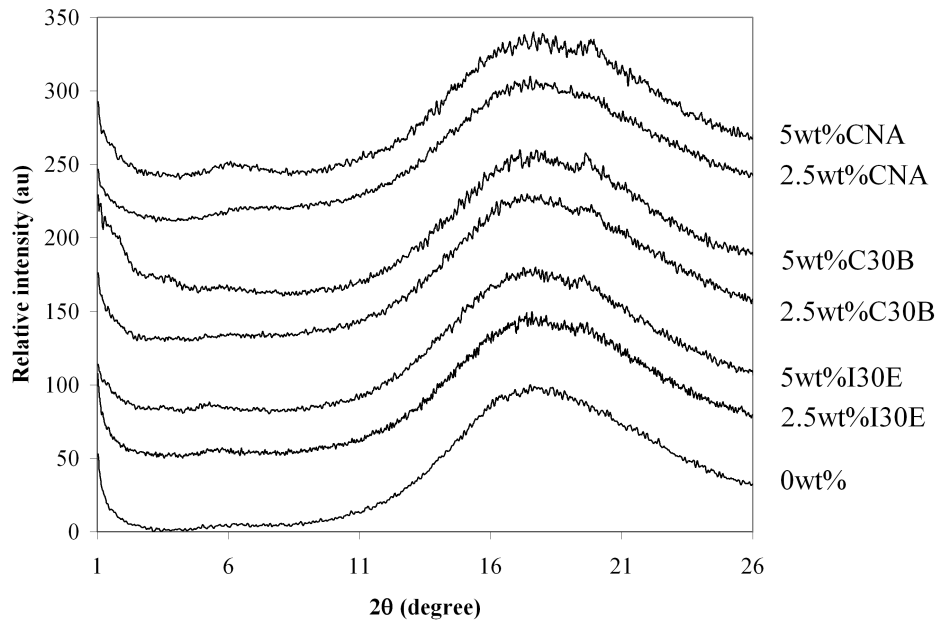
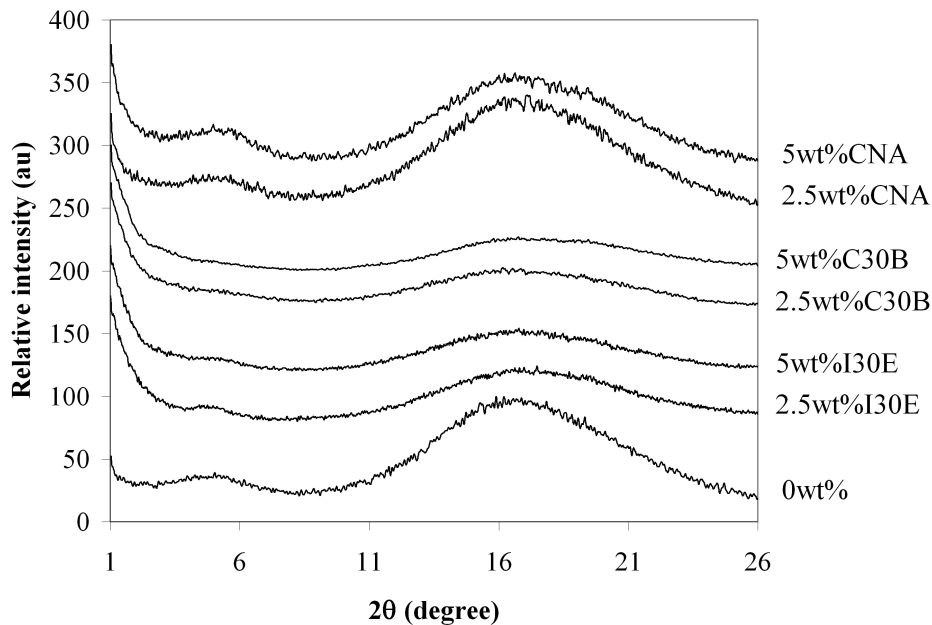**Figure 3(a). Reflected XRD patterns of MMT-epoxy nanocomposites**

Figure 3(b). Transmittted XRD patterns of MMT-epoxy nanocomposites

compared to the unfilled epoxy [16]. In contrast, in the CNA-epoxy systems, the CAN clay particles do not change the morphology of the system. This result together with DSC results confirmed that this untreated clay does not swell and react chemically with the epoxy. This also suggests that even though the reflected XRD pattern is a common tool to determine the structure of nanocomposites, the reflected XRD pattern by itself was not quite accurate and may provide false information.

A typical micrograph of a clay-epoxy nanocomposite is shown in Figure 4. Figures 4a, 4b and 4c shows the TEM images of 2.5wt%I30E-epoxy, 5wt%C30B-epoxy and 2.5wt%CNA-epoxy nanocomposites respectively. TEM images of

2.5wt%I30E-epoxy and 5wt%C30B-epoxy materials exhibit a number of parallel organoclay layers. It was calculated that the average layer distance was between 6.1 – 11.1 nm and 10.7 – 11.5 nm and a minimum layer distance of 2.5 nm and 3.5 nm for I30E-epoxy and C30B-epoxy respectively.

This indicates that these materials possess a mixed structure of exfoliated and intercalated structures, where exfoliation is at best partial. In contrast, based on the 2.5wt%CNA-epoxy nanocomposite image, the organoclay layers are not separated, but form bulk areas in the epoxy and built a conventional composite material. It is clear, once again, that natural clays do not swell with the epoxy.
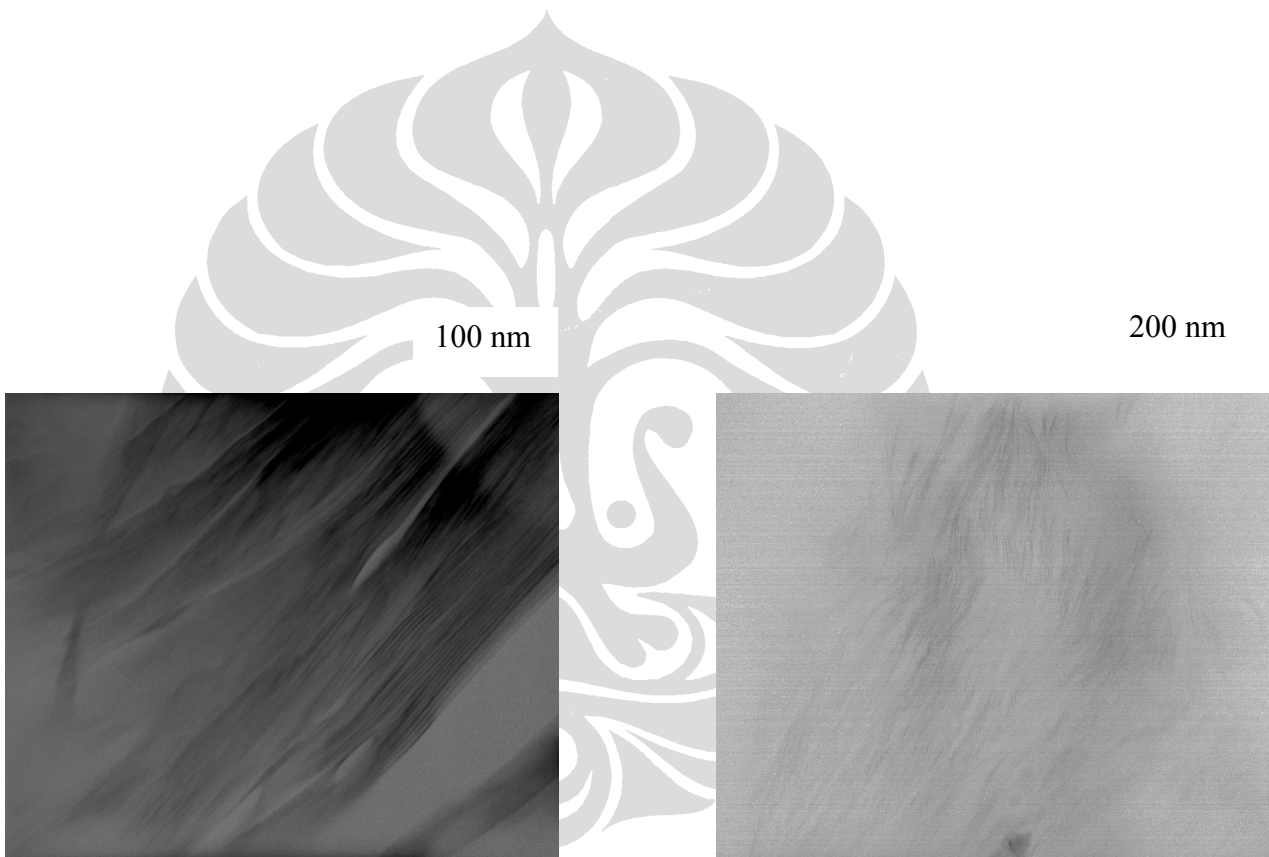
100 nm

200 nm

Figure 4(a). TEM image of 2.5wt%I30E-epoxy nanocomposite

Figure 4(b). TEM image of 2.5wt%C30B-epoxy nanocomposite
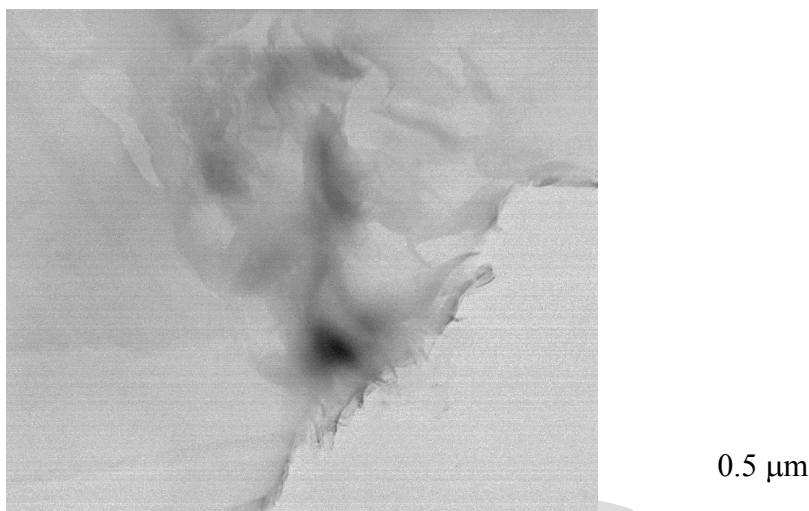
0.5 μm

Figure 4(c). TEM image of 2.5wt%CNA-epoxy composite.

4. Conclusions

MMT-epoxy materials were successfully synthesized by in-situ polymerisation. Six MMT-epoxy systems were produced from two organoclays, namely I30E and C30B, and an unmodified clay, namely CAN; and two different clay loadings; 2.5wt% and 5wt% for each system. It is well established that reflected XRD and DSC analysis are popular tools to study the clay-epoxy materials. However, this study shows that the reflected XRD patterns of the organoclay – epoxy and unmodified – epoxy exhibit similar results. More over, the DSC analysis of MMT-curing agent-DGEBA samples demonstrated one peak for all samples. In contrast the transmitted XRD patterns of the organoclay – epoxy and unmodified – epoxy exhibit different results as well as the DSC analysis of MMT-DGEBA samples exhibits different patterns between the organo clay – epoxy and unmodified – epoxy materials. In conclusion, the transmitted XRD and DSC analysis of clay-epoxy mixture are also important to determine the property of the materials. The TEM observation is not the only tool to determine the structure because the intercalation structure may not be distinguished clearly with the micro composite structure.

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