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The effect of Clay Structures on the Modification Process to Synthesize Polymer-Clay Nanocomposites

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Abstract

Over the past decade, organoclays have been a subject of high interest within the scientific community and industry. Using such materials combined with polymeric resin to synthesize Polymer-Clay Nanocomposites (PCN) is proposed to enhance the corrosion protection performance of the resin along with the mechanical and thermal properties. Clays have to be treated before being introduced to the targeted polymeric resin. The structure of clays plays a major role in determining the efficiency of the treatment process to synthesize well-functioning organoclays. In this paper, an in-depth investigation was conducted to correlate the structures of two different clays, bentonite and kaolinite, to the efficiency of the treatment process. Cationic exchange reaction was used to produce organoclay for PCN synthesis. X-ray diffraction (XRD), flame photometry and scanning electron microscopy (SEM) were used to identify the response of these two clays to the cationic exchange reaction. It has been concluded that such reaction is significantly effective with 1:2 layered silicate clay (Bentonite) while it has not shown any effect on the 1:1 layered silicate clay (Kaolinite).

1. Introduction

Polymeric materials have been widely used in the industry with applications in the polymeric coatings. Generally, unpigmented coating cannot stand the severity of the environment where the coating is used. Permeation of some aggressive species through the coating can lead to undesirable results. Sometimes, unpigmented coating shows poor ionic resistance, which is considered one of the main factors that have to be improved. Poor ionic resistance can be a result of the presence of pores, defects, and areas of poor cross linking. In this case, water, oxygen, and some other species will find a route to permeate. Consequently, the corrosion process will have a high possibility to start under the coating leading to failures in the coating. Nanotechnology has been introduced to increase the resistance of the coating by implementing nano-layers inside the coating. It is believed that these layers have the ability to act as physical barriers that reduce the diffusion rates of the corrosive species through the coating. These barriers are silicate layers and they are classified as nano-pigments. Such treated coating is considered to be a composite material and it is preferably named layered silicate nanocomposite. The main two components determining the efficiency of PCN are the resin and the silicate layers that can be extracted from mineral clays. There are many types of clays that consist of silicate sheets in their chemical structure, although only a few types can be treated to be active and can interact with the resin. As it will be shown later in this paper, there is a critical condition that has to be present in the clay structure to be possibly treated. Two different types of clays were involved in this research to fully understand the conditions and the mechanisms of interaction between the clay and the resin. The two clays are kaolinite and bentonite, which have a similar chemical nature with a few differences. Bentonite belongs to a group of clays classified as 2:1 layered or phyllosilicates having the chemical formula of $Al_2O_3.5SiO_2.6H_2O$. The crystal structure consists of layers made of two tetrahedral silicon sheets fused to octahedral sheet of aluminium hydroxide [1]. The layer thickness is around 1 nm, and the lateral dimensions of these layers may vary from 30 nm to several microns or larger. Stacking of the layers leads to a regular gap between each adjacent silicate layer called the interlayer or gallery. The layers in bentonite are negatively charged and they are counterbalanced by alkali and alkaline earth cations situated inside the galleries. Kaolinite, also known as China clay, is a hydrated aluminium silicate mineral having a chemical formula of $Al_2O_3.2SiO_2.2H_2O$ [2]. Its chemical structure is similar to bentonite, but the main difference is that kaolinite is classified as 1:1 layered or phyllosilicates. Accordingly, its structure consists of one tetrahedral silicate sheet bonded to one octahedral sheet of aluminium hydroxide by hydrogen bonds [3,4]. Comparing the two types of clays, bentonite is a three-layer aluminium silicate, consisting of an octahedral aluminium layer sandwiched in between two layers of tetrahedral silicates. The three layers are held together covalently by hydrogen bonds forming a three-layer sandwich. The sandwiches are held together by relatively weak Van Der Waals force. Another important difference is that, between the sandwiches, there are alkali and alkaline earth cations [5]. The clay is a cheap, readily available and eco-friendly mineral with high surface area and it is widely used as reinforcement for the polymer and in the drilling fluids industry [6-11]. The proposed technique to prepare PCN is based on mixing the clays with polymeric resin. However, direct physical mixing does not form the desired PCN with the required properties. The main purpose of using clays as pigments is that the silicate layers in these materials should exfoliate and disperse within the resin. As mentioned earlier, the silicate layers in bentonite are held together by weak Van Der Waals forces while hydrogen bonds are holding the layers in kaolinite. In the case of a direct physical mixing, the layers might not disperse due to the mentioned forces. For this reason, a pre-treatment process should take place to weaken the forces holding the structure [4]. To achieve a successful dispersion, a reaction known as cation-exchange reaction has been proposed to treat the structure of the clay [14]. Pristine bentonite usually contains Na^+ or Ca^+ cations while kaolinite does not. In the proposed treatment process, cations-exchange reactions between the clay and cationic surfactants will take place to replace the cations. The most important function of the intercalating agents is to penetrate into the clay layers to modify its surface by decreasing its hydrophilicity [15-20]. This could improve the dispersion process of the layers after being mixed with the resin [20]. The later mentioned treatment process is basically an intercalating process that leads to increasing the spacing and to lower the adhesion forces between the silicate layers. The amine has the ability to achieve such target by acting as an intercalating agent. The most widely used intercalating agents are the alkylammonium cations molecules because the amine function can be easily protonated in an acidic medium. Additionally, the amines are thermally stable and provide large variety when it comes to alkyl chains length. The efficiency of the intercalating agents is mainly influenced by the agent’s properties such as the hydrocarbon chain length. A more realistic description has been proposed by Vaia based on Fourier transform infrared spectroscopy experiments [21]. It was found that the degree of increase in the spacing between the layers depends on the length of hydrocarbon chain [1].

2. Experimental details

2.1. *Materials*

Two types of clays were used in the preparation of epoxy based PCN coatings: Sodium-Bentonite and Kaolinite were obtained from CTM Company, U.K. The intercalating agents used in the experiments to treat the clays were dodecylamine and hexadecylamine, which were purchased from Alfa Aesa. Hydrochloric acid (HCl) with a mass fraction of 37% was used in this study. The polymer used in this work was a commercial epoxy paint supplied by HMG, Ltd and known as Epilife. This consists of a two-component system of which the resin is an epoxy adduct containing approximately 20% xylene solvent and the hardener is an amine adduct.

2.2. Preparation of Organoclays

The modification of the clays was performed using cationic exchange reaction. The silicate layers had to be intercalated by using a solution containing alkylammonium cations. Two different intercalating agents were used to produce four different modified materials: Bentonite + dodecylammonium chloride (BD), bentonite + hexadecylammonium chloride (BH), kaolinite + dodecylammonium chloride (KD) and kaolinite + hexadecyl-ammonium chloride (KH). The above four materials were made using the same method based on the following procedure: two different solutions were prepared and were designated as S1 and S2. The preparation of S1 involved the addition of 4.41 g of dodecylamine or 5.75 g of hexadecylamine and 2.4 mL of HCl solution were thoroughly mixed into 100 mL of distilled water and stirred at 70°C for 1 hour. At this stage, a solution having a concentration of 0.238 M of the intercalating agent was prepared. 10 g of bentonite or kaolinite were dissolved into 200 mL of deionized water and stirred at 70°C for 3 hours. Then, the solution S1 was added dropwise to solution S2 at a rate of 10 mL per minute. The resulting solution was then stirred and heated for 1 hour at 70°C to afford a white precipitate. This precipitate was filtered and washed with hot water and filtered again. This process was repeated several times to make sure that the residues of the ammonium salts were completely removed.

2.3 *Preparation of PCN*

Five different polymers were prepared and evaluated: Unpigmented epoxy, unpigmented epoxy treated with BD (CBD), unpigmented epoxy treated with BH (CBH), unpigmented epoxy treated with KD (CKD), and unpigmented epoxy treated with KH (CKH). The epoxy was mixed with the hardener based on a ratio of 3:1 for 10 min. Then, it was cured at room temperature for 24 hours. For 1% loadings, four different PCNs, CBD, CBH, CKD, CKH, were prepared using the same procedure. 21g of the unpigmented epoxy and 0.28g of the desired treated clay were mixed on a hot plate for three hours. The mixing procedure was done vigorously using a magnetic stirrer. After that, the solution was cooled at room temperature overnight while it was stirring. Then, 7g of the hardener was added and the solution was mixed aggressively before being cured. The PCN containing treated clays at 3 and 5 wt% loadings were prepared using the same procedure; the loadings were 0.84 and 1.4g, respectively.

2.4 Flame Photometry

The main purpose for conducting this experiment was to analyze the filtered solution produced from synthesizing the organoclays. The reason for using the amines to treat the clays was to increase the space between the layers in the structure of the clay to make it possible for the polymeric resin to interact with the clay after mixing. The treatment process was mainly based on a chemical reaction involving cations exchange between the prepared protonated amines and the cations in the clay structure. Based on this fact, the filtered solution mentioned in section 2.2 is considered to be an indicator that confirms the cations exchange process. In this experiment, 100 mL of solution was taken from each filtration process and was examined by the flame photometry instrument. The main setup of this instrument consists of the main pump used to drive the solution from the sample’s reservoir to the flame generated by using methane. The instrument was equipped with a specific filter that is used to identify sodium. The filter is connected to a detector to measure the intensity of the radiation emitted due to agitating the sodium elements. The detector can then measure the concentration of sodium present in parts per million (ppm). To properly analyze the data, a calibration curve was generated to correlate the intensity of the radiation to the concentration of a given element. Based on that, a solution of sodium with a concentration of 1000 ppm was diluted to several known concentrations. Then, each known concentration was examined by the instrument to determine the equivalent intensity reading.

2.5 X-Ray Diffraction Experiments

X-ray diffraction patterns were obtained at room temperature using a Philips diffractometer, type PW 3710, with programmable control unit and nickel filtered Cu-Kα radiation in Bragg–Brentano geometry (Θ–2Θ). In this experiment, glass samples were used and two samples were prepared for each PCN. The glass material was selected due to its amorphous structure, which reduced the sources of interference that would affect the results. The glass samples had a dimension of 2.5 × 7.5 cm and were coated using the same procedure mentioned earlier.

2.6 Scanning Electron Microscope

The morphology of the prepared PCN was evaluated using Philips 505 scanning electron microscope operated at 20 kV. The substrate used was aluminium with a dimension of 1.5 × 2 cm, and it was coated by the prepared PCN. The surface of the PCN was gold coated to make it possible to distinguish between the prepared PCN and the resin (Araldite) filling the mould (sample holder). The gold coating was cured at room temperature for three hours. Each sample was fixed to a holder and was placed into a cylindrical mould with a 3 cm diameter. The Araldite resin and its hardener were mixed and put into the mould. Then, the mixture was cured for 24 hours at room temperature. The prepared specimens were grinded using 240, 320, 400, 600, 800, 1200 and 4000 grade silicon carbide paper. They were cleaned with distilled water, ethanol, and acetone.

3. Results and Discussion

3.1 Flame Photometry

A flame photometer was used to identify the cations present in the structure of the clays and it was used to evaluate the performance of the intercalating agents. Sodium cations were the main cations expected to be present based on the data sheet obtained from the supplier. For this reason, this experiment was mainly involved to trace sodium. According to the experimental procedure explained in in section 2.4, 100 mL was taken from the filtered solution obtained during preparing the organoclays. The amount measured in the 100 ml solution does not represent the actual amount present in the clay, but it describes the performance of the agents used.

Table 1: Solution analysis obtained from treatment of bentonite.

Type	Reading	Amount, ppm (diluted)	Amount, ppm (solution)
Bentonite	19	5.5	55
BD	56	20	200
BH	70	30	300

Table 2: Solution analysis obtained from treatment of kaolinite.

Type	Reading	Amount (ppm)
Kaolinite	7	2
KD	6	1.9
KH	6	1.9

Table 1 shows two different solutions, diluted and concentrated. The diluted solution was made to make it possible to measure the concentration from the calibration curve. Then the values measured were corrected to measure the actual concentration present in the 100 mL sample. The dilution process was carried out by diluting 10 mL obtained from the desired sample in 100 ml deionized water. The data obtained for kaolinite showed that there was almost no interaction between the agents and the clay. This is clear from Table 2 shows that the same amount of sodium was detected before and after treatment. This result was expected because the structure of kaolinite does not show any presence of cations inside the clay. Studying the structure of kaolinite before and after the treatment can provide a solid confirmation, which would conclude the absence of any interaction. Consequently, it can be concluded that the treatment process has not been successful in the case of kaolinite. Table 2 reveals some critical observations which shows the difference between the agents used. It is clear from the data obtained that the amount of sodium has increased after introducing the agents. In the case of dodecylamine, 200 ppm of sodium was detected showing that the presence of such agent enhanced the extraction of sodium. The increase in the concentration reveals that the agent supported the cations exchange reaction. This shows that the protonated amine diffused inside the silicate layers to cause an increase in the distance between the layers. Thus, this kind of interaction should give a chance for more cations to leave the clay's structure to be detected in the filtered solution. In the case of hexadecylammonium, it was observed that a higher sodium concentration was detected. This observation is supported by the assumption that the difference in the chain length helped the hexadecylammonium to significantly increase the distance between the layers giving a chance for more sodium to leave the clay structure. A larger distance between the layers will considerably help to provide better interaction between the modified clays and the epoxy resin. Based on these results, it can be concluded that hexadecylammonium offers an effective treatment compared to the other agent.

3.2 X-Ray Diffraction

X-ray diffraction was performed to verify the exfoliation of the silicate layers in the epoxy resin. Out of this experiment several main aspects are considered such as the spacing between the silicate sheets inside the clay, the degree of intercalation, the agglomeration of non-reacted clay as well as the change in the clay microstructures due to the presence of the intercalating agents. Figure 1 shows X-ray diffraction patterns of bentonite, the modified bentonite with hexadecylammonium, and of the modified bentonite with dodecylammonium.

Small-angle X-ray scattering was performed; 2θ is from 0 to 12, which shows (001) reflection corresponding to the repeat distance perpendicular to the silicate layers. During the analysis of the XRD results, three main factors were carefully monitored including the position of the peak, the full width at half maximum of the peak, and the intensity of the peak. The analysis shows a change in the (001) basal reflection in bentonite after the treatment process using two different agents. In the case of using dodecylamine, there is a clear shift in the (001) reflection peak to a lower angle. At the same time, the new reflection peak showed an increase in the intensity and a decrease in the peak width. It is documented that a decrease in the degree of coherent layer stacking (which means a more disordered system) results in peak broadening and intensity loss. It was reported that the surface roughness, composition, and sample alignment can disturb the shape of the peak [22-24]. Based on that, it can be predicted that the protonated dodecylamine has interacted with bentonite to increase the spacing between the silicate layers from 11 to 17 Angstrom. Such findings reveal that the efficiency of such chemical to intercalate the clay is about 54%, which supports the main hypothesis that this study is based on.

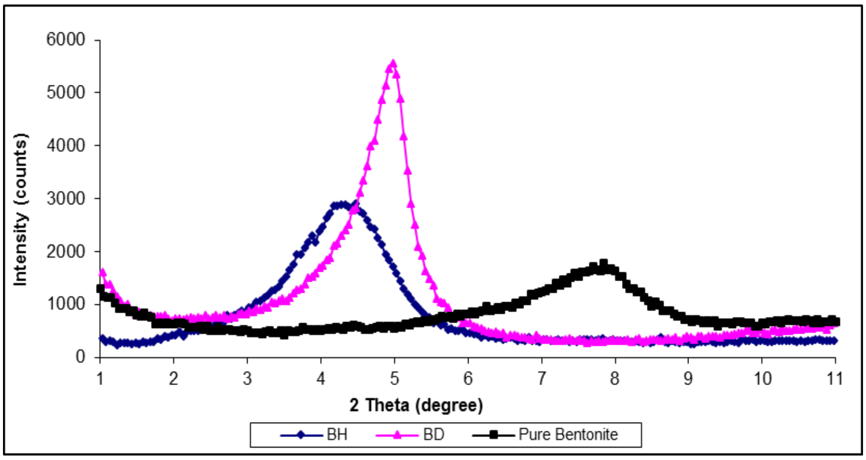

Figure 1: The XRD spectra obtained for Bentonites samples

It can be found that the presence of the protonated dodecylamine increased the internal structure order of bentonite. Such intercalation can be considered to be a significant modification in the clay, which makes it possible to synthesize a PCN. For the protonated hexadecylamine, an intercalating efficiency of about 85% was achieved. A decrease in the intensity and an increase in the peak width compared to the protonated dodecylamine were noticed. Comparing the two intercalating agents, the protonated hexadecylamine has shown a better performance as an intercalating agent. For kaolinite, Figure 2 shows the X-ray diffraction patterns for pure kaolinite and modified kaolinite with protonated dodecylamine.

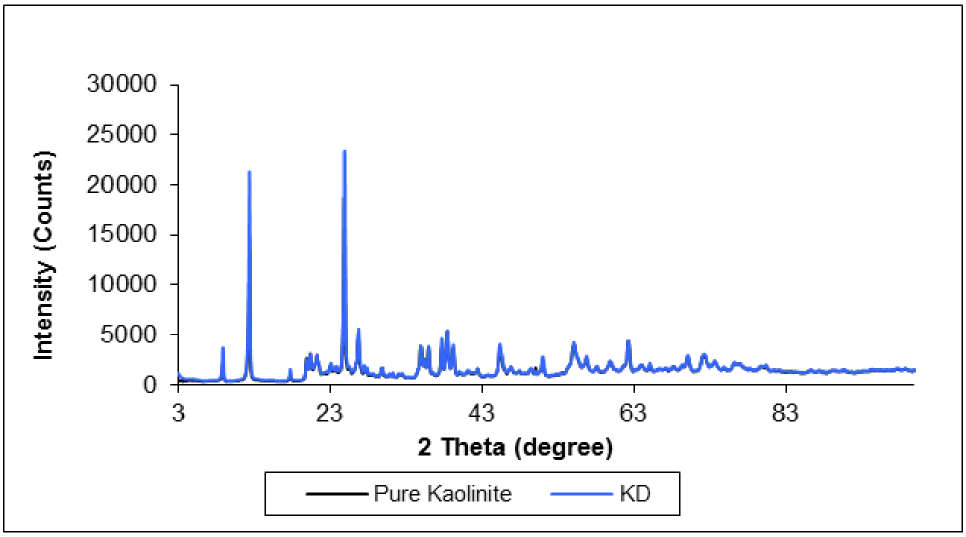

Figure 2: The XRD spectra obtained for kaolinite samples

A wide range of *2θ* shows that the two spectrums (before and after treatment) have a high degree of similarity. There is little deviation at a very low angle, but this is due to the instrument and not related to the structure. A comparative plot for both chemicals is shown in Figure 3 at a small angle scale:

As it is clear from Figure 3, a very high degree of similarities is noticed for kaolinite before and after treatment. This means kaolinite did not interact with the intercalating agents and consequently will not form any kind of PCN. The reason for that is the microstructure of kaolinite does not support the treatment process as mentioned before. To study the changes in the internal structure of the clays after mixing with epoxy resin, each prepared resin was examined by XRD and the results obtained are shown in Figures 4 and 5.

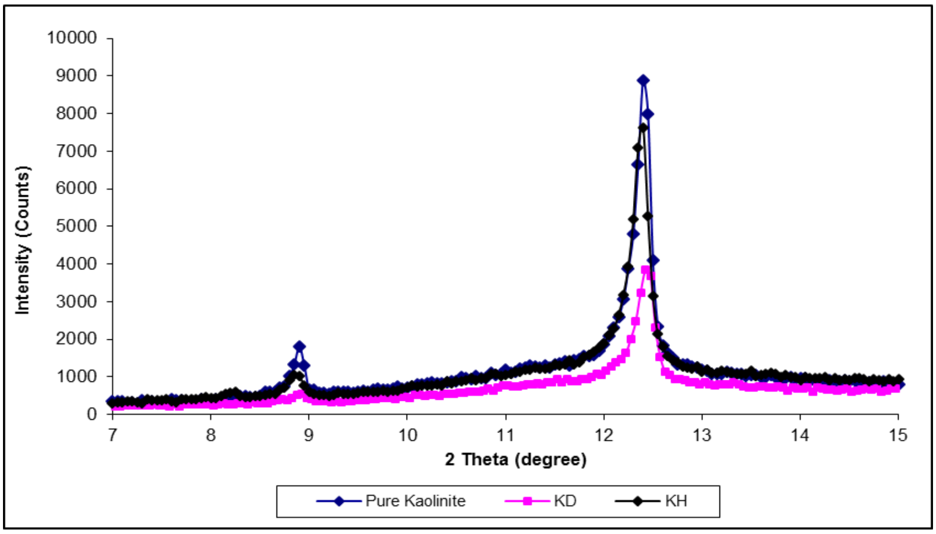

Figure 3: The XRD spectra obtained of kaolinite samples

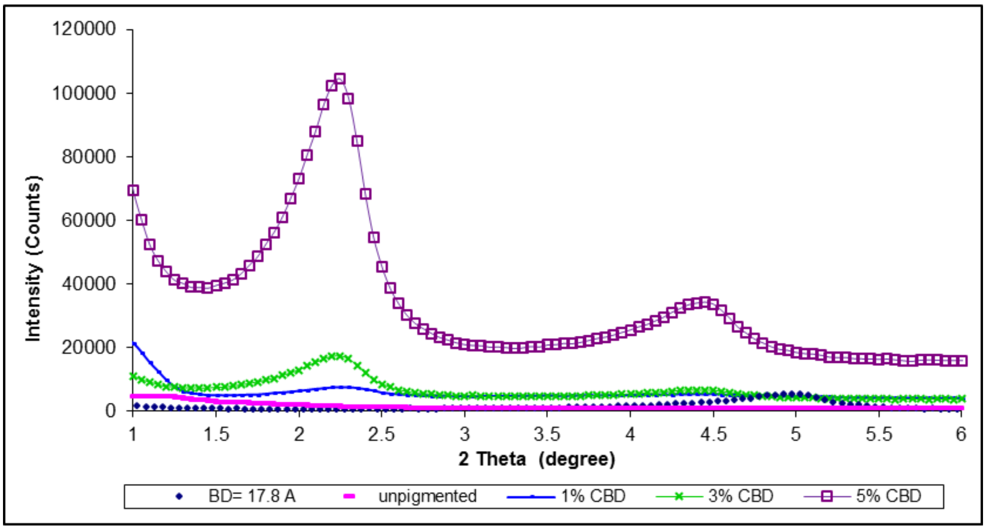

Figure 4: The X-ray diffraction spectra of CBD samples

In this experiment, only the clay inside the epoxy was detected and not the epoxy itself. Some of the treated clay was slightly intercalated and was present as phase 1 and an intercalated bentonite was observed inside the polymer as phase 2. By observing Figure 4, 1%, 3% and 5% loading show two different diffraction peaks at the same position. The first one was at $2\theta = 4.5^{o}$, which is very close to the diffraction peak shown by the treated bentonite. This shows that the clay inside the polymer was slightly intercalated by the epoxy. At $2\theta = 2.3^{o}$, stronger peaks were observed for each polymer indicating that the epoxy was involved in an intercalation process of the clay and these peaks got stronger as the clay loading increased. Based on that, three main phases were expected inside the polymer. This are slightly intercalated clay that could be observed by the XRD, and the exfoliated clay that could not be seen by the XRD. The first two phases introduced agglomerated areas inside the polymer and acted as sites where the polymer linkage was discontinued forming weak sites. Figure 5 showed the result obtained for CBH PCN. The first peak was observed at the same position as the treated Bentonite. The intensity of the peaks was very low and sometimes, the peak is almost not there as it was observed in the case of 1% CBH. The intensity of the peak can also provide information about the number of the layers per crystallite [17]. The decrease in the intensity compared to CBD means that the number of the silicate layers are less than in the case of CBD. This can support the fact that stronger exfoliation behaviour could be achieved in CBH. It is also noticed that the second phase was in the position as the CBD, but the peaks were noticeably weaker. This data suggests that BH gave the possibility for the epoxy to intercalate the clay to form better intercalated PCN compared to the CBD. This fact can be attributed to the better performance observed in the case of hexadecylamine. For the epoxy treated with kaolinite, the following results were obtained:

The XRD data for the treated and pure kaolinite suggest that mixing kaolinite with the epoxy resin will not form any kind of PCN and will act only as fillers inside the polymer. After mixing the kaolinite with the epoxy, no intercalating process was observed and the XRD curves obtained for all types of CKD and CKH showed a significant similarity to the one obtained for the pure kaolinite.

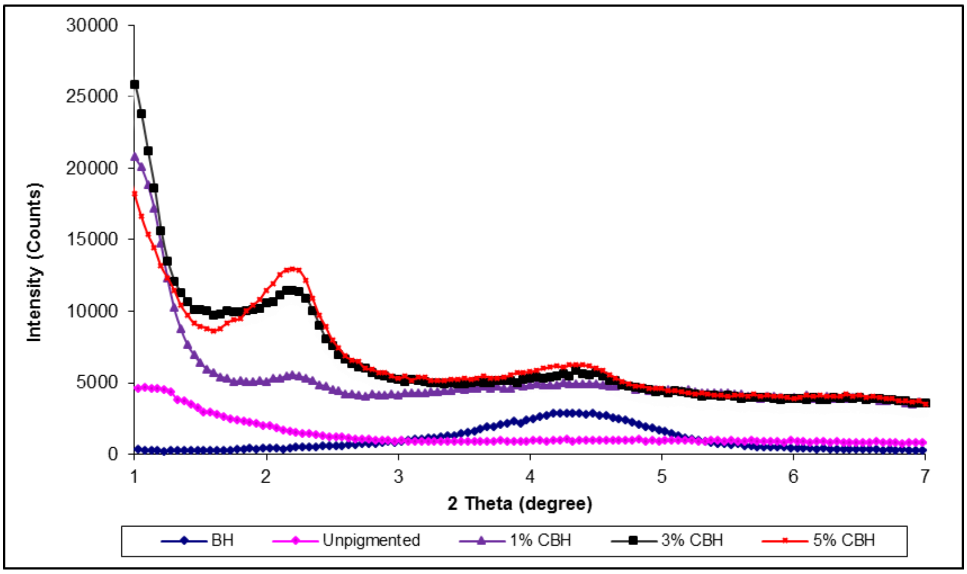

Figure 5: The X-ray diffraction spectra of CBH samples

Figures 6 and 7 show that there are two main diffraction peaks at the positions 12.5 and 9, which are the peaks identifying the pure kaolinite. In fact, adding kaolinite to epoxy might even introduce some agglomeration areas that might weaken the polymer as a coating system. It must be noticed that the intensity of the reflection peak in the case of kaolinite increased after treatment. It was also noticed that when the treated kaolinite was mixed with epoxy resin, the positions of the reflection peaks have not changed despite the change in the intensity. It is believed that during kaolinite treatment, the agents are absorbed on the surface of the kaolinite. This makes such a surface more hydrophobic and will change the length of the Si-O in the structure. Consequently, a change in the layer stacking is expected due to the change in the length of such a bond. An increase in the intensity of such peaks suggests that more stacking in the layers is expected [25,26].

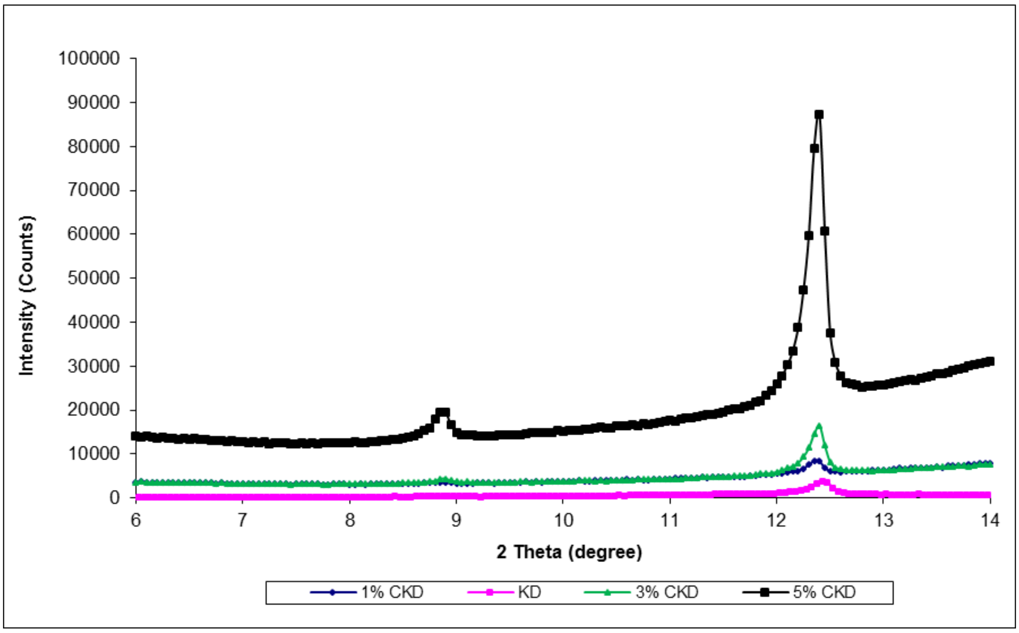

Figure 6: The X-ray diffraction spectra of CKD samples

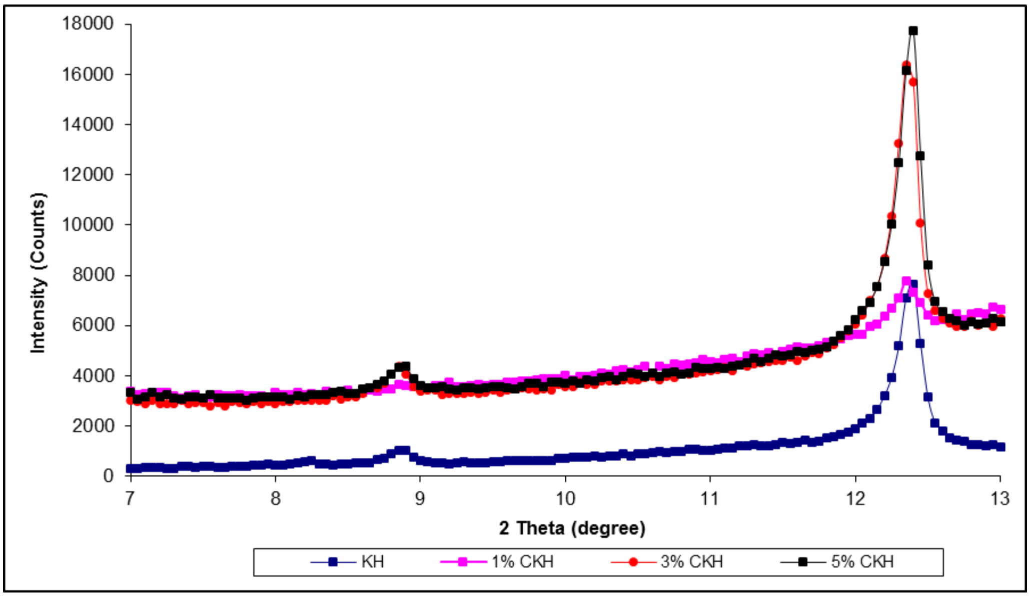

Figure 7: The X-ray diffraction spectra of CKH samples

3.3 Scanning Electron Microscope

All prepared polymers were examined using SEM and shown in Figures (8-19). The main objective of this technique was to study the behavior of the clay after being added to the resin.

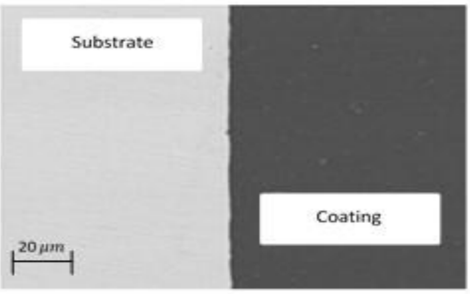

Figure 8. SEM image for 1% CBD

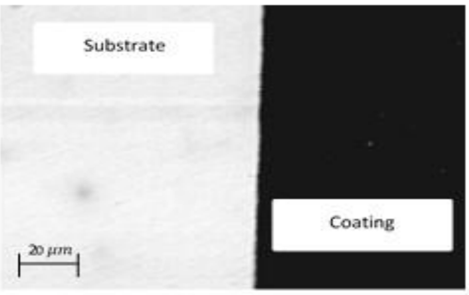

Figure 9. SEM image for 3% CBD

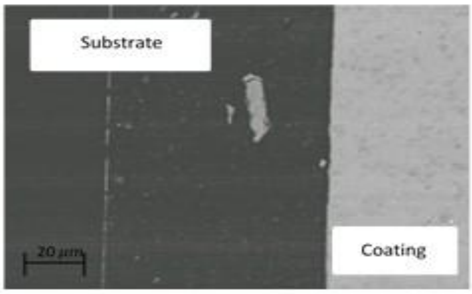

Figure 10. SEM image for 5% CBD

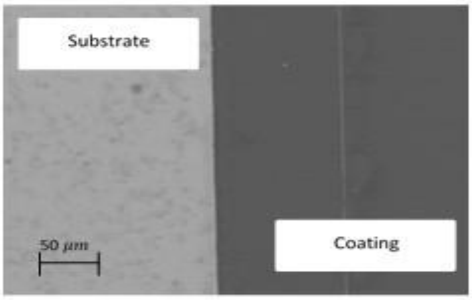

Figure 11. SEM image for 1% CBH

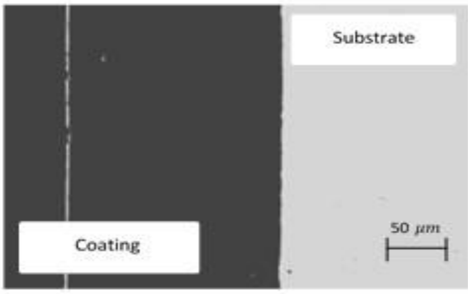

Figure 12. SEM image for 3% CBH

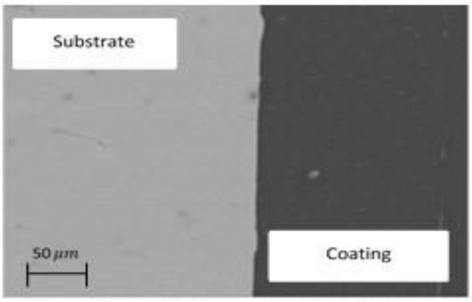

Figure 13. SEM image for 5% CBH

Based on the XRD data, the clays might form several phases that could have great influence on the performance of the polymer. The SEM was used mainly for qualitative analysis which was done to analyze the agglomerated areas. The SEM images show that there are three main sections that can be distinguished. These sections represent the substrate, the prepared polymer layer, and the resin used to prepare the sample.

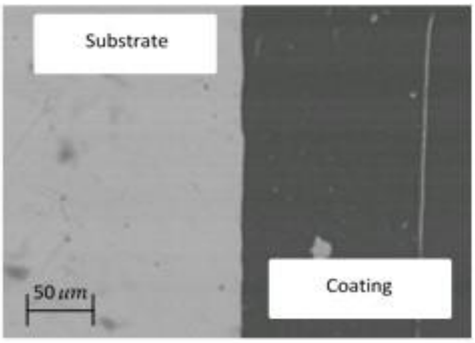

Figure 14. SEM image for 1% CKD

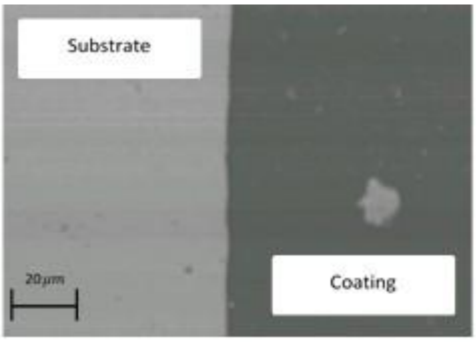

Figure 17. SEM image for 1% CKH

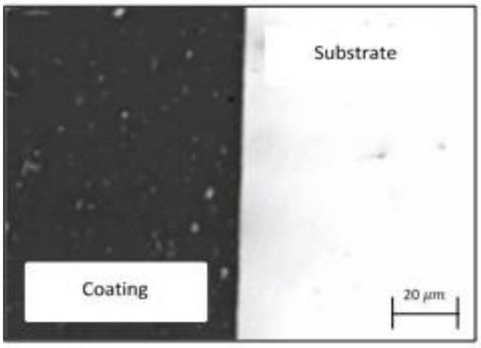

Figure 15. SEM image for 3% CKD

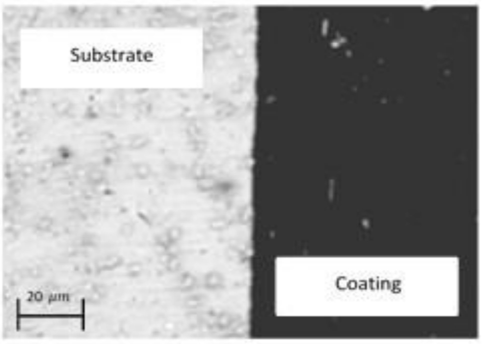

Figure 18. SEM image for 3% CKH

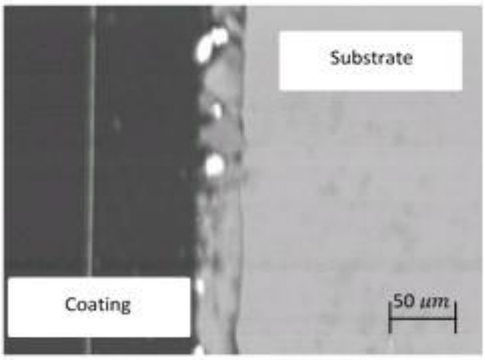

Figure 16. SEM image for 5% CKD

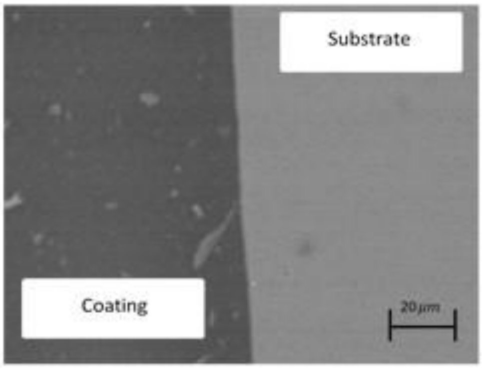

Figure 19. SEM image for 5% CKH

The area of the prepared polymer was distinguished from the area representing the resin by a bright line, which is a gold coating that was implemented for this purpose. By investigating the SEM images of the Bentonite-PCN, in Figures (8-13), bright areas were detected in some sites in the polymer layer. In both types of PCN, the degree of these areas increased as the loading of the clays increased. These areas can be defined as an agglomeration inside the polymer as will be confirmed later by the EDS analysis. It is believed that these agglomerated sites are attributed to the non-reacted phases of the clays. Comparing CBH and CBD, the CBD showed a higher level of agglomeration and larger areas of clustering. In a careful study of the SEM result obtained for 5% CBD, Figure 11, a large clustered area was detected. Such large agglomeration can significantly decrease the efficiency the polymer as a coating. The obtained results for polymer treated with kaolinite, Figures (14-19), showed similar behavior but with a higher agglomeration level. The XRD results suggest that the kaolinite was not intercalated by the amine and consequently the kaolinite did not interact with the epoxy resin. Based on that, most of the kaolinite added was distributed in the polymer to form clusters. This finding can be proven by comparing 5% CBH and 5% CKD. The results show a high level of unreacted clay in the case of 5% CKD while insignificant clusters were detected for 5% CBH. These bright areas seen by the SEM are considered to be from the clays. To confirm this fact, scanning electron microscopy and energy dispersive spectroscopy (SEM/EDS) were carried out to identify such areas.

Figures (20-23) show the chemical analysis conducted to analyze the second phase observed in both 3% CKH. The 3% CKH sample was selected to represent the polymer treated with kaolinite. It was believed that the bright phase detected was due to the presence of the clay. Based on that, it was believed that carrying out the EDS analysis on one sample only will be sufficient to identify the phase found. During the chemical analysis, two different points were selected on the polymer; the first one was on a spot where the bright phase can be seen on the Figures 21 and 22, while the other one was away from the phase as Figures 23 and 24 show. The data showed the phase contains mainly silicon, aluminium, oxygen, and carbon. Analyzing this finding reveals that, these bright areas are clays that have not interacted with the resin. This finding is supported by the detection of silicon and aluminium, which are the main constituents of clay, were detected. The presence of carbon was due to the carbon coating used to prepare the sample, while the oxygen signals were due to the presence of oxygen in the epoxy coating and the clay itself. The analysis of the second point showed that carbon and oxygen are mainly present with very little amount of silicon, aluminium and chloride.

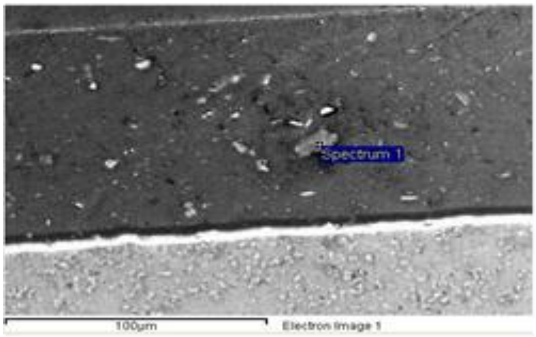

Figure 20. SEM/EDS for 3% CKH (point 1)

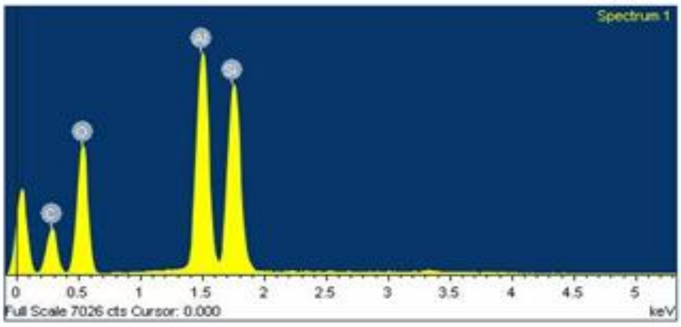

Figure 21. SEM/EDS for 3% CKH (point 1)

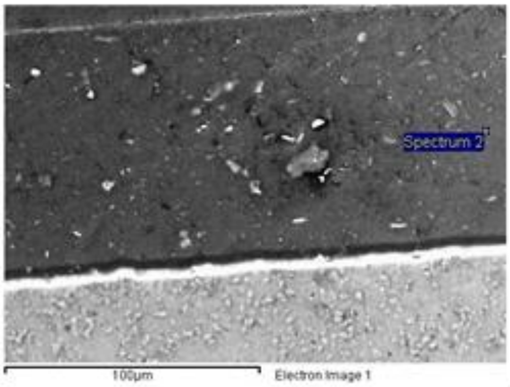

Figure 22. SEM/EDS for 3% CKH (point 2)

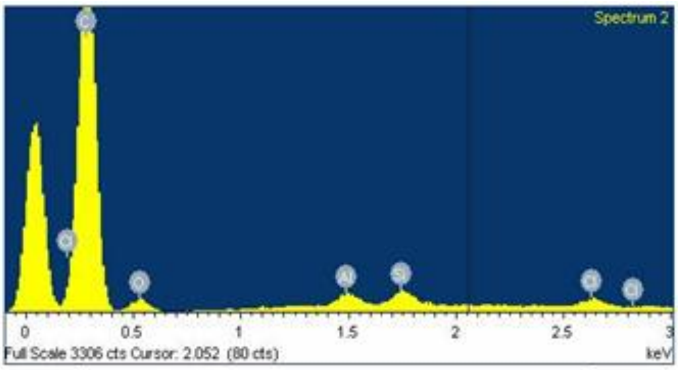

Figure 23. SEM/EDS for 3% CKH (point 2)

Conclusion

In the present work, we have shown that the incorporation of modified clay in the formulation of epoxy-based coatings resulted in the development of epoxy/clay nanocomposites with intercalated structures. To ensure proper exfoliation of the clay materials within the resin a proper treatment procedure had to be followed. It has been found that the exfoliation level is highly influenced by the clay structure and the intercalating agent used to modify the clay by cationic exchange reaction. The obtained results confirmed that the hypothetical mechanism of the treatment process is feasible and the Kaolinite did not support the cations exchange reaction. This finding indicates that the presence of Kaolinite in the epoxy resin doses not form any kind of epoxy/clay nanocomposites. Finally, the difference in the chain length between the agents had a great influence on the quality of the organoclays. The synthesized polymer-clay nanocomposites can be used as coatings for corrosion protection, acting as physical barriers to reduce the diffusion rate of water through the organic coatings. The use of clays fillers in epoxy polymer matrices opens the door to designing new generation of polymeric materials with enhanced properties. These properties include mechanical performance, thermal stability and flame retardancy. When these materials are enhanced, they become promising for many applications such as the automotive industry, energy and packaging sectors. Further studies in the application of these materials are underway in our laboratory.

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