

## Increasing the D-Spacing of Kaolinite to Intercalate PMMA/Kaolinite Nanocomposites

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**Abstract :** Nanocomposite material which contains inorganic nanolayer clay and organic polymer has attracted considerable attention in recent years. Particularly, intercalation of organic polymer into inorganic layered host lattice has approved to be an effective way to construct inorganic–organic nanosystem. A layer silicate of composition  $Al_2Si_2O_5(OH)_4$ , from Aldrich Company (Germany) with a diameter of  $5–10\mu m$  is reported. Kaolinite treated by dimethylsulfoxide (DMSO) as an aqueous system to expand the interlayer basal spacing. The basal spacing was increased from 7.15 to 11.2 Angstrom by using X-ray powder diffraction (XRD). The analyses made by using XRD shows kaolinite spacing before modification is 0.715 nm while it became in the range of 0.715 nm – 1.12 nm. This result conforms to that of transmission electron microscope, which shows the same order of magnitude in the range of nm. . In this study, eight nanocomposites were formed; one set contains four different ratio of (kaolinite/DMSO)/PMMA, while the other contains that of PMMA and pristine kaolinite.

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### I. Introduction

Study the intercalation of Polymethyl methacrylate in the clay mineral kaolinite and the ability of XRD and TEM to characterize the produced nanocomposite, also compare between the pure kaolinite and modified kaolinite nanocomposite.

Previous studies confirm that it is possible to modified and enhance the properties of kaolinite through another of methods by mean of polymer clay nanocomposite and characterization by another of technique. Yoshihiko Komori in (1999) stated that Alkykamines and water were intercalated between the layers of kaolinite by utilizing a kaolinite/methanol intercalation compound as an intermediate. [1] A kaolinite/methanol intercalation compound was synthesized by guest displacement reaction of a kaoliniterN-methylformamide intercalation compound with methanol. The basal spacing increased up to 5.75 nm when octadecylamine was used. It increased linearly with the length of alkyl chains by 0.255 nm per carbon atom, suggesting that the alkylamine molecules in the interlayer space of kaolinite take a bilayer arrangement with their alkyl chains almost perpendicular to the layers of kaolinite. Water molecules were also intercalated into kaolinite by displacement of methanol. The basal spacing of the product was 1.00 nm under wet conditions and 0.85 nm after drying. By using hydrated kaolinite as an intermediate, pyridine molecules were intercalated into kaolinite, thus, the hydrated kaolinite also shows the ability as an intermediate for displacement reactions. These results demonstrate that kaolinite has higher intercalation ability for a wider variety of guest species. [1]

Llu's Cabedo in (2004) used novel route to develop EVOH-kaolinite nanocomposites by a melt intercalation process and on some relevant nanocomposite properties as a function of composition. [2] The kaolinite clay used is a very cheap raw material of the tile industry and as such needed to be refined and chemically modified prior to the melt intercalation step. The modification was carried out with dimethylsulfoxide, methanol and octadecylamine in order to increase the basal plane distance of the original clay by a factor of more than three. Melt blended nanocomposites were characterized by WAXS, TEM, DSC, TGA and oxygen transmission rate. Partial exfoliation and intercalation of the clay platelets was the dominant morphology attained. An increase in thermal resistance, glass transition temperature, crystallinity and barrier properties to oxygen were also observed for mass clay loadings below 8%. [2]

Kayode O. Adebawale in (2005) proved that the modification of kaolinite clay mineral with orthophosphate (p-modified sample) enhanced adsorption of Pb and Cd ions from aqueous solutions of the metal ions. Increasing pH of solutions of metal ions, increasing adsorbent dose and increasing concentration of metal ion, increased the adsorption of metal ions. Adsorption of both metal ions simultaneously on both unmodified and p-modified samples indicates that adsorption of one metal ion is suppressed to some degree by the other.

Ca-electrolytes had more negative effect on the adsorption capacities of the adsorbents than Na-electrolytes. Ca-electrolytes reduced adsorption capacities of the adsorbents for Pb and Cd ions. From Langmuir plots it was observed that these electrolytes increased the binding energy constant of the metal ions unto the adsorbents especially on the p-modified samples. The rate of adsorption of Pb and Cd ions on p-modified adsorbent were increased and equilibrium of metal ion solution were more quickly reached (8 min for Pb ions and 12 min for Cd ions) with p-modified adsorbent as against 20 min for adsorption of both metal ions on unmodified adsorbent when 200 mg/L of metal ion solutions were used during the kinetic studies. [3]

Yin-Lin Wang in (2007) developed three types of polymer-kaolinite nanocomposite resins (C(K-diamine), C(K-acrylamide), and C(K-acetate)) with the potential to provide sustained release of fluoride due to the strong adsorption of kaolinite to fluoride during the fabrication process. Their mechanical (hardness, flexural strength, flexural modulus, fracture toughness, and diametral tensile strength) and fluoride release properties were investigated. X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) analyses demonstrated that hexanediamine, acrylamide, and ammonium acetate were successfully intercalated into the interlamellar structure of all three resins. Of the three types of polymer-kaolinite nanocomposite resins, C(K-acrylamide) exhibited the greatest mechanical strength and greater fluoride release than Fuji IX. In addition, C(K-acrylamide) released more fluoride than Fuji IX and Z-100 after exposure to 0.2% NaF. It is concluded that C(K-acrylamide) can potentially serve as a useful restorative material with caries-preventive properties. [4]

Yanfeng Li, in (2007) display that polymethyl methacrylate-kaolinite intercalation composites were prepared by making use of intercalation method. Thus crude kaolinite (K0) was sequentially modified with dimethylsulfoxide (DMSO)-methanol (MeOH) and potassium acetate (KAc)-aqueous systems to expand the interlayer basal spacing. Then the organic molecules-modified kaolinite (K2) was used as clay precursor to synthesize the PMMA-kaolinite intercalation composites via in situ polymerization of methyl methacrylate (MMA) in the presence of benzoyl peroxide (BPO). The resulting different intercalation composites were characterized by means of X-ray powder diffraction (XRD), X-ray photoelectron spectroscopy (XPS), attenuated total reflection-infrared spectroscopy ATR-FTIR, scanning electron microscopy (SEM), thermogravimetric analysis (TGA), differential thermal analysis (DTA), ultraviolet (UV) absorbance experiments. At last, the mechanical and aging resistance properties of different kinds of compounds were tested. [5]

Tamer A. Elbokl in (2008) showed that the intercalation of two cyclic imides, succinimide and glutarimide, in the interlayer spaces of kaolinite was obtained from a "soft guest-displacement method" by displacing previously intercalated guest molecules. The dimethyl sulfoxide (DMSO)-kaolinite preintercalate was particularly efficient for that purpose. [6]

The intercalation exchange was done from a concentrated aqueous solution of the cyclic imides, at ambient temperature, in a relatively short time. Complete displacement of DMSO by the cyclic imides was confirmed by the results of several independent characterizations, including XRD, TG/DTA, FTIR, and <sup>13</sup>C MAS NMR analyses including dipolar dephasing experiments. The results of the TG/DTA analyses showed enhanced thermal stabilities of the imide intercalates compared with the starting materials. These results demonstrate the potential use of kaolinite as a slow-releasing agent for molecules structurally related to the cyclic imides of this study. [6]

Emerson H. de Faria in (2009) presents the results of the functionalization of Brazilian kaolinite with pyridine-2-carboxylic and pyridine-2,6-dicarboxylic acids. The functionalization involved refluxing of the pyridinecarboxylic acid in the presence of kaolinite previously intercalated with dimethyl sulfoxide; both acids effectively displaced dimethyl sulfoxide from the clay interlayer. The resulting materials were characterized by X-ray diffraction, thermal analysis, infrared absorption spectroscopy, and C and N elemental analysis. The X-ray diffractograms revealed the incorporation of the acid molecules into the interlayer space of kaolinite. The thermogravimetric curves of the kaolinite samples functionalized with the pyridine-carboxylic acids indicated that the materials were thermally stable up to 300<sup>0</sup>C . The displacements of the bands due to interlayer hydroxyls in the infrared absorption spectra also confirmed the functionalization of the kaolinite with the pyridine-carboxylic acids. [7]

Ray L. Frost ;J. Theo Klopogge in (2006) , study the intercalation of a number of organic molecules in kaolinite, a 1 : 1 clay mineral which is generally assumed not to swell, is described along with the influence of these molecules on the clay internal and external surfaces. The reactive molecules are inserted between the successive kaolinite layers, thereby disrupting the hydrogen bonds between the hydroxyl groups on one side and the oxygen atoms of the siloxane layer on the other side. The organic molecules will form new bonds with either the more hydrophobic siloxane layer or with the more hydrophilic hydroxyl groups. In this article, the intercalation of molecules such as hydrazine, urea, formamide, acetamide, DMSO and acetate are discussed. Extensive infrared and Raman spectroscopic research has resulted in a much more detailed picture of how these organic molecules are incorporated in the kaolinite structure. [8]

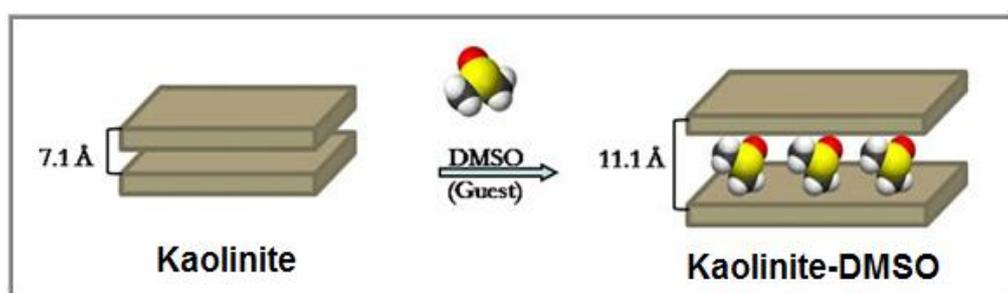
## II. Experimental Procedure

In this study, the intercalation of Poly(methyl methacrylate) into kaolinite is the main target. Poly(methyl methacrylate) was mixed with kaolinite directly, and also mixed after modification of kaolinite by DMSO, using the ultrasonic oscillations.

The ultrasonic oscillations can also affect the microstructure of clay, causing more regions of exfoliated clay. Due to better dispersion of clay and smaller crystal size, the elongation at break of polymer/layered nanocomposites ultrasonically treated was greatly increased; meanwhile ultrasonic oscillations also improved their other mechanical properties, such as tensile and impact strength.

### Preparation of kaolinite/ DMSO

Kaolinite–DMSO intercalate was typically prepared by mixing 9gram of kaolinite with 60 mL of DMSO in a sealed container for a sufficient time (72 hour) with occasional stirring to achieve maximum intercalation. A representation of this process is shown in figure (1). The product was vacuum-filtered and washed with ethanol for three times to remove excess DMSO and then air-dried to yield an off-white powder.



**Fig.1** Intercalation of organic molecules (DMSO) in kaolinite

### Preparation of PMMA/kaolinite intercalation nanocomposites

Different ratios of PMMA and pure kaolinite were mixed with different ratios as listed in table (1).

**Table (1)** The ratio of PMMA and kaolinite mixed

No	Kaolinite %	PMMA %
1	95	5
2	80	20
3	70	30
4	60	40

0.2 g of PMMA was taken from the first mixture (with ratio 5:95) and solved in 50 mL of chloroform using magnetic stirring for about 30 min or until the polymer become soluble. In the other side, 3.8 g of kaolinite with 50mL of chloroform was put in the ultrasonic for one hour. After that, clay was put in magnetic stirring and drops of PMMA were added to achieve a good intercalation. The produced powder was dried in oven with  $60^{\circ}C$  for about 24 hours. The other ratios were treated by the same manner.

### Preparation of PMMA/(kaolinite + DMSO) intercalation nanocomposites

The modified kaolinite was mixed with PMMA in the same ratios that were mixed without modification. In this series of experiments, Kaolinite was prepared by the displacement of DMSO with polymer. (3.8 g) of Kaolinite /DMSO mixture and an aqueous solution of PMMA (0.2g) was stirred for one hour, then the product was dried in dry oven for 24hour, washed with ethanol, and air-dried to yield nanocomposite.

### Sample characterization

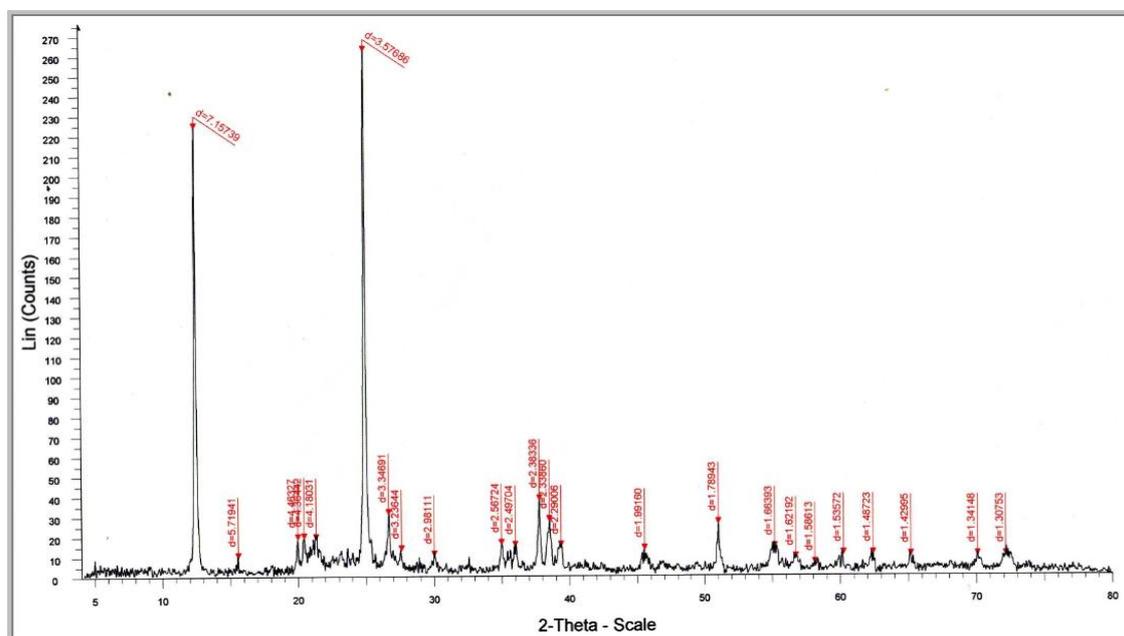
PMMA/kaolinite was characterized by different techniques XRD, TEM. These instruments were used to confirm that good intercalation was achieved, through the change in the spectrum which is the real indication for this intercalation.

## III. Results And Discussion

### X-Ray Diffraction for samples

To calculate the clay d-spacing, Bragg's law ( $\lambda = 2d \sin \theta$ ) was applied. Typical X-ray powder patterns of the starting materials (kaolinite) is shown in figure (2), (Kaolinite–DMSO) pattern is shown in figure (3), and the PMMA film is shown in figure (4). The X-ray pattern of resulting PMMA/(Kaolinite–DMSO)

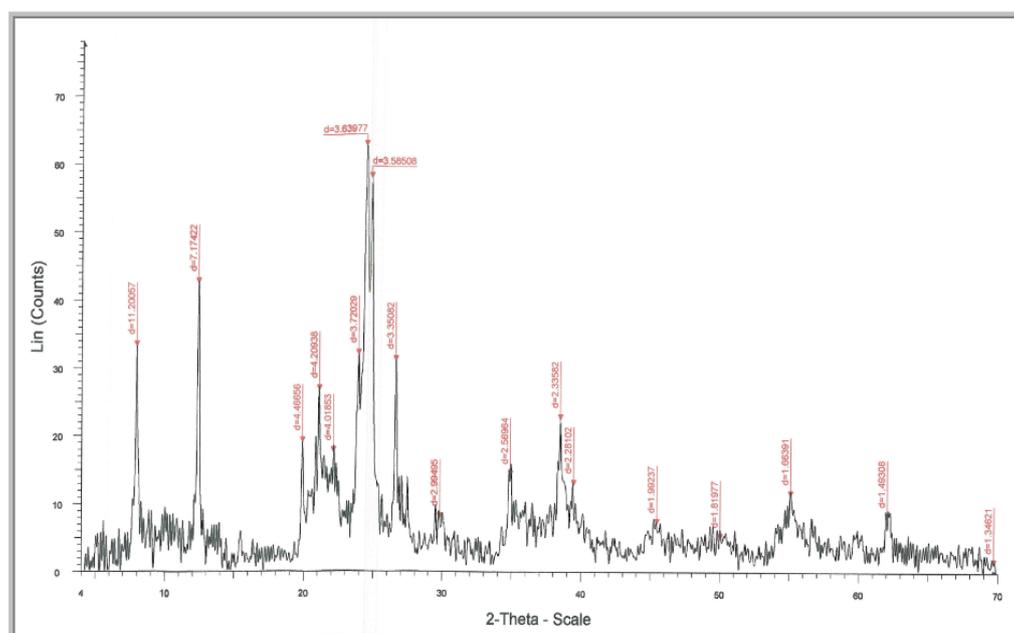
nanocomposites are shown in figures from (5) to (8), and the X-ray pattern of the PMMA/Kaolinite nanocomposites are shown in figures from (9) to (12) for the range of  $2\theta = 0 - 70^\circ$ .



**Figure (2)** X-Ray diffraction pattern of Kaolinite

**Table (2)** the angle, d-value and intensity of kaolinite

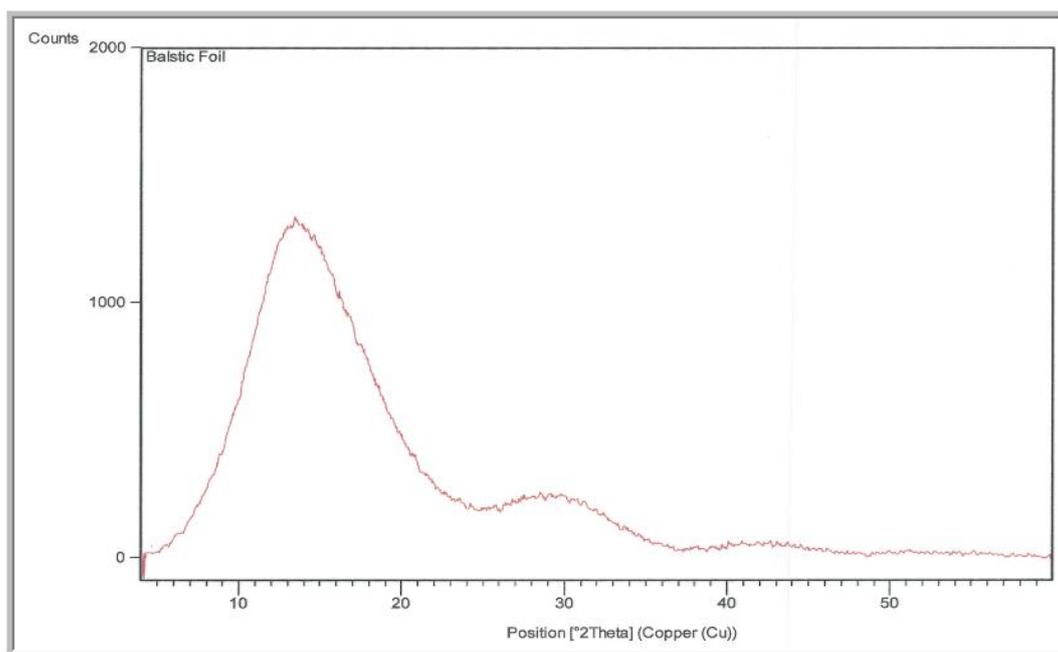
Angle (2theta)	d value (Angstrom)	Intensity of reflection (a.u.)	Intensity (%)
12.357	7.15739	225	85.3
15.48	5.71941	9.11	3.5
19.876	4.46327	18.3	6.9
20.331	4.36442	18.6	7.1
21.237	4.18031	18.2	6.9
24.873	3.57686	263	100
26.612	3.34691	30.6	11.6
27.538	3.23644	12.4	4.7
29.95	2.98111	9.76	3.7



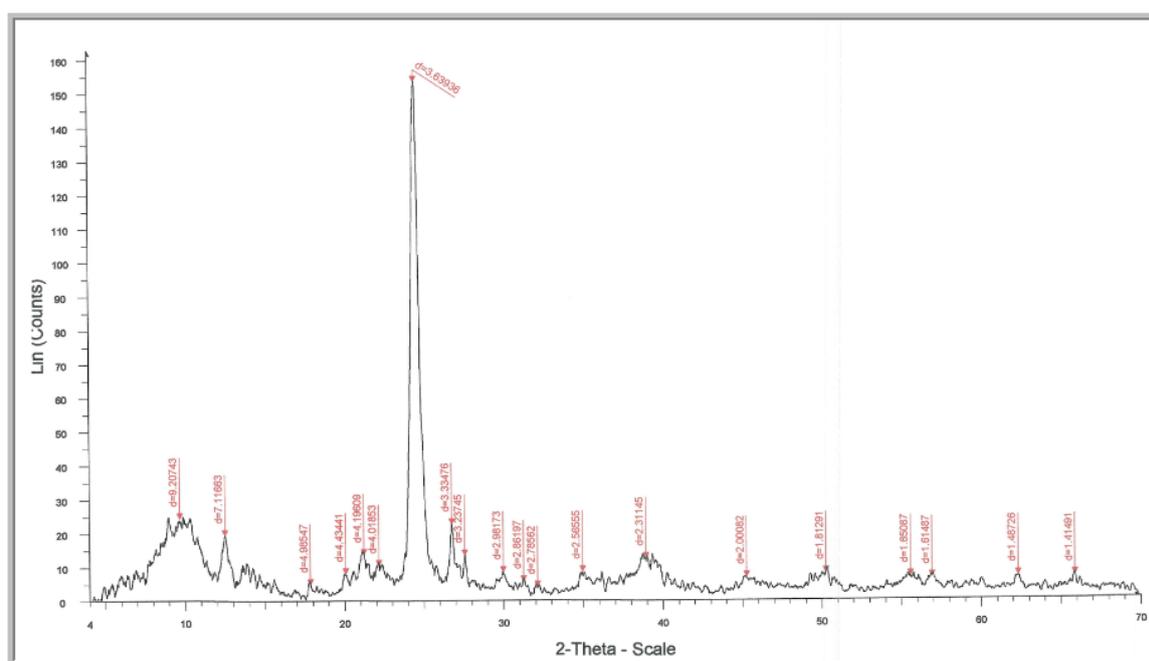
**Figure (3)** X-Ray diffraction pattern of Kaolinite+DMSO

**Table (3)** The angle, d-value and intensity of kaolinite+DMSO

Angle (2theta)	d value (Angstrom)	Intensity of reflection (a.u.)	Intensity (%)
7.887	11.20057	33.2	53
12.328	7.17422	42.6	68
19.862	4.4665	18.8	30
21.089	4.209	26.7	42.6
22.103	4.0185	17.4	27.9
23.899	3.720	31.8	50.8
24.436	3.639	62.6	100
24.815	3.5850	57.9	92.4
26.581	3.35082	30.9	49.4
29.808	2.9949	7.67	12.2



**Figure (4)** X-Ray diffraction pattern of PMMA



**Figure (5)** X-Ray diffraction pattern of 95% (kaolinite/DMSO) 5% PMMA nanocomposite

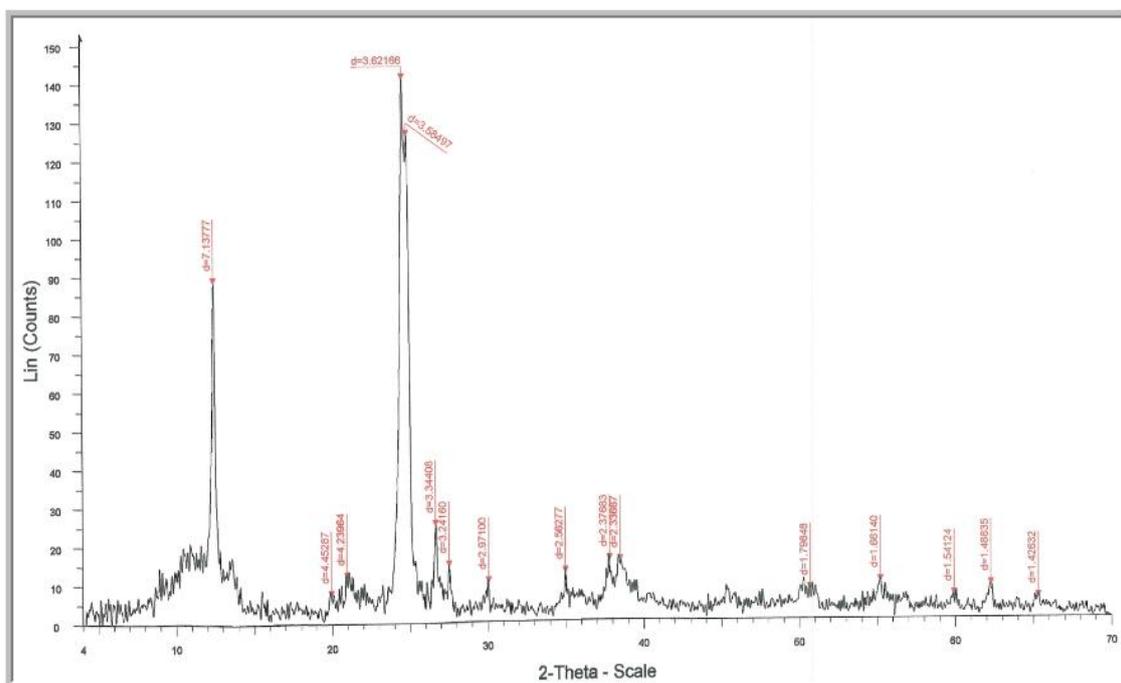


Figure (6) X-Ray diffraction pattern of 80 % (kaolinite/DMSO) 20% PMMA nanocomposite

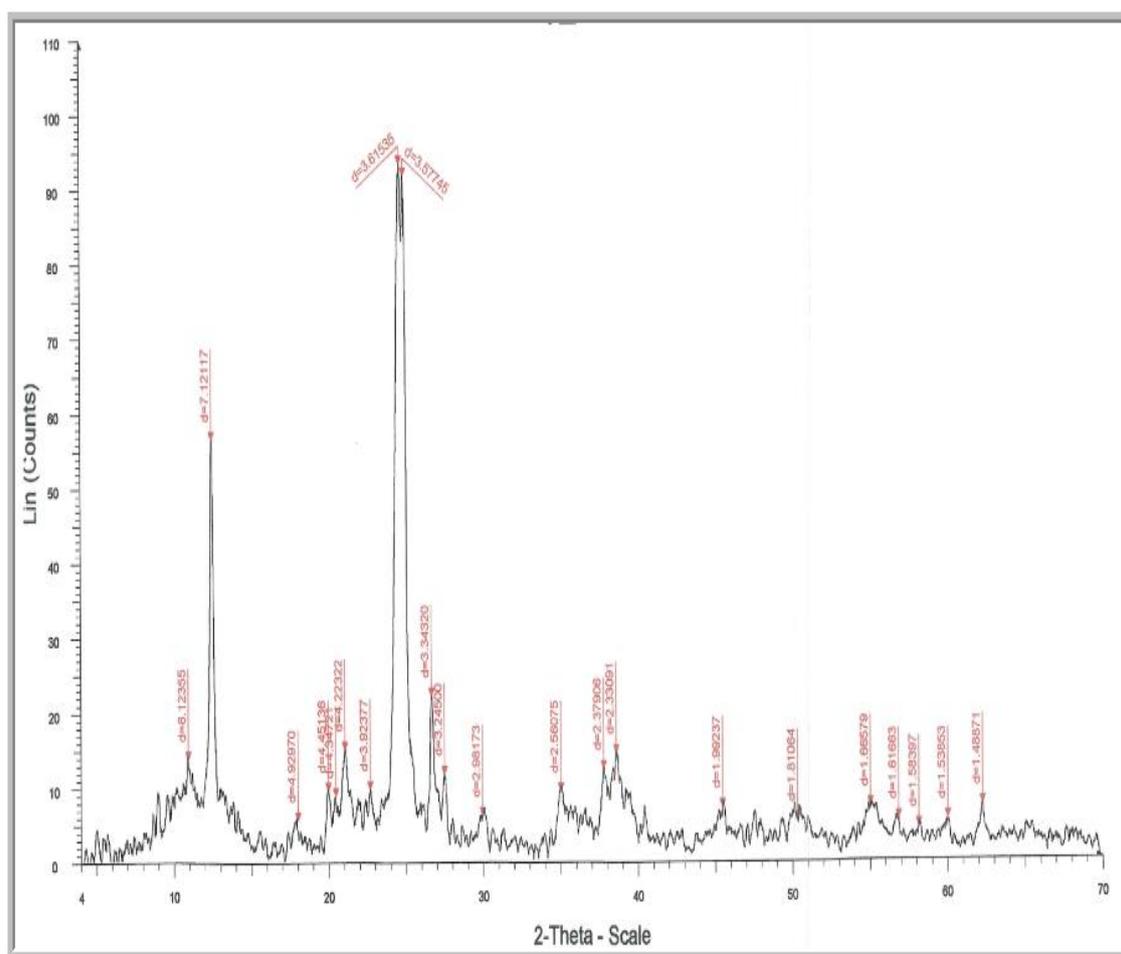


Figure (7) X-Ray diffraction pattern of 70% (kaolinite/DMSO) 30% PMMA nanocomposite

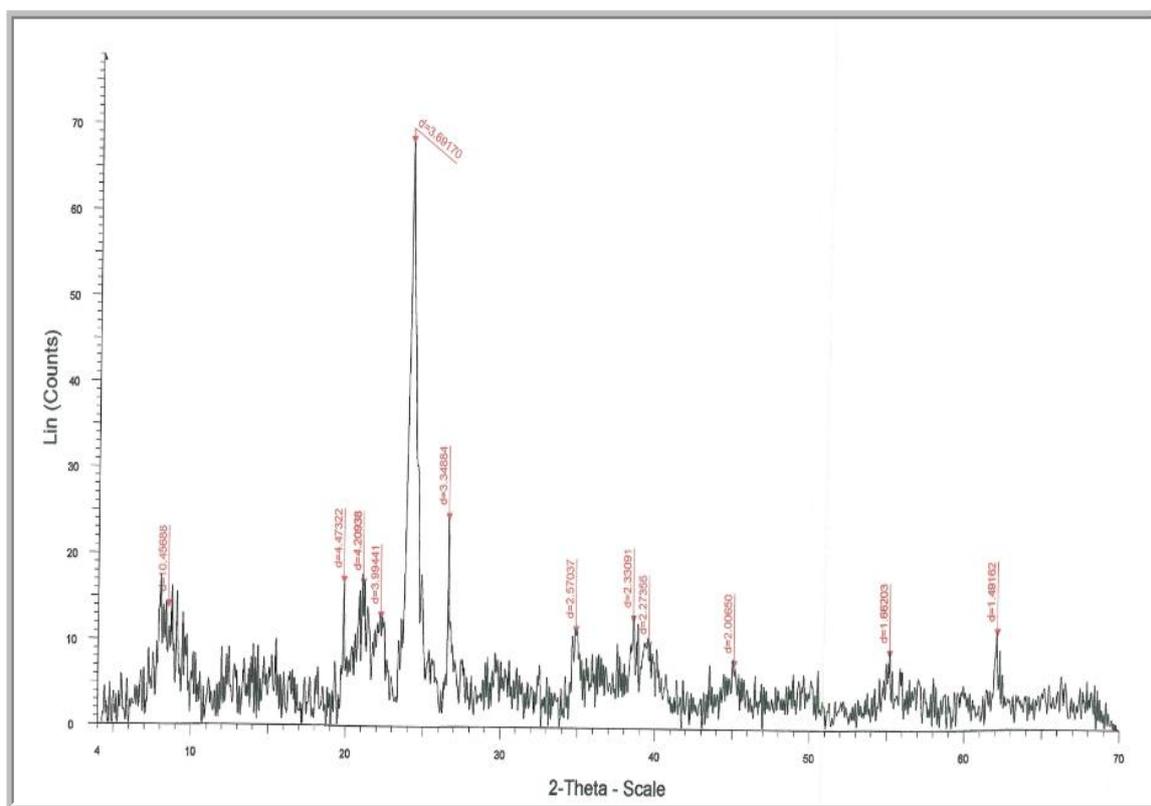


Figure (8) X-Ray diffraction pattern of 60 % (kaolinite/DMSO) 40% PMMA nanocomposite.

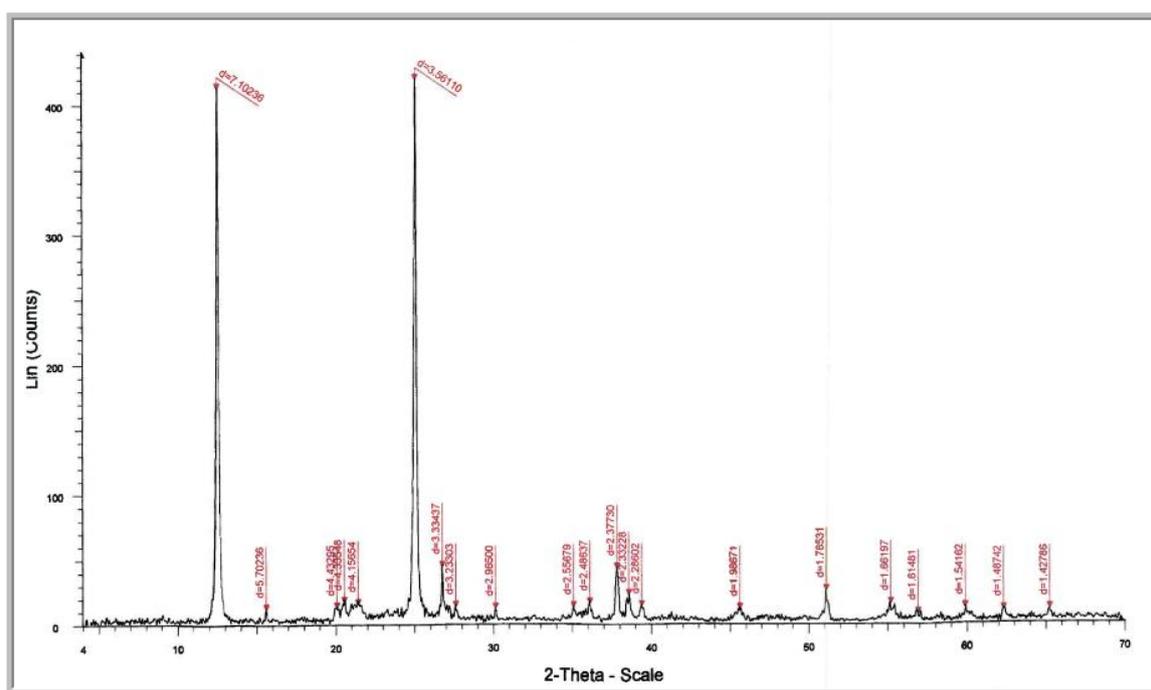


Figure (9) X-Ray diffraction pattern of 95% kaolinite/ 5% PMMA nanocomposite

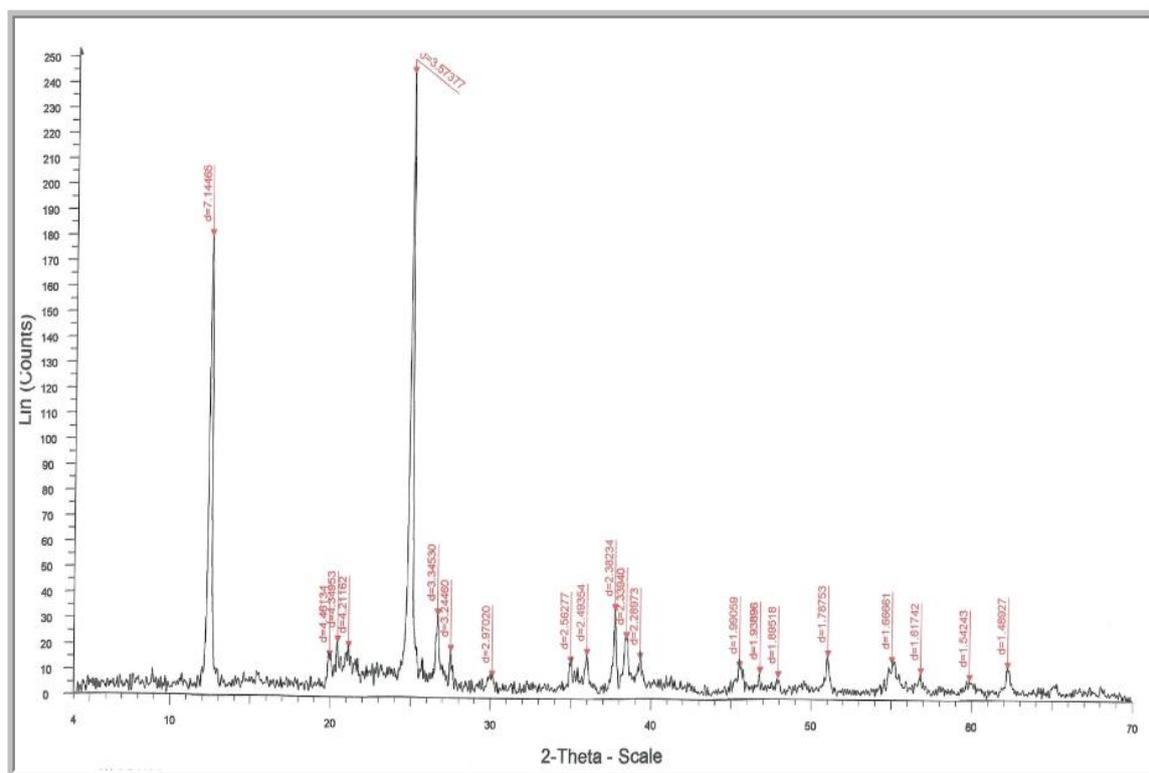


Figure (10) X-Ray diffraction pattern of 80%kaolinite/ 20%PMMA nanocomposite

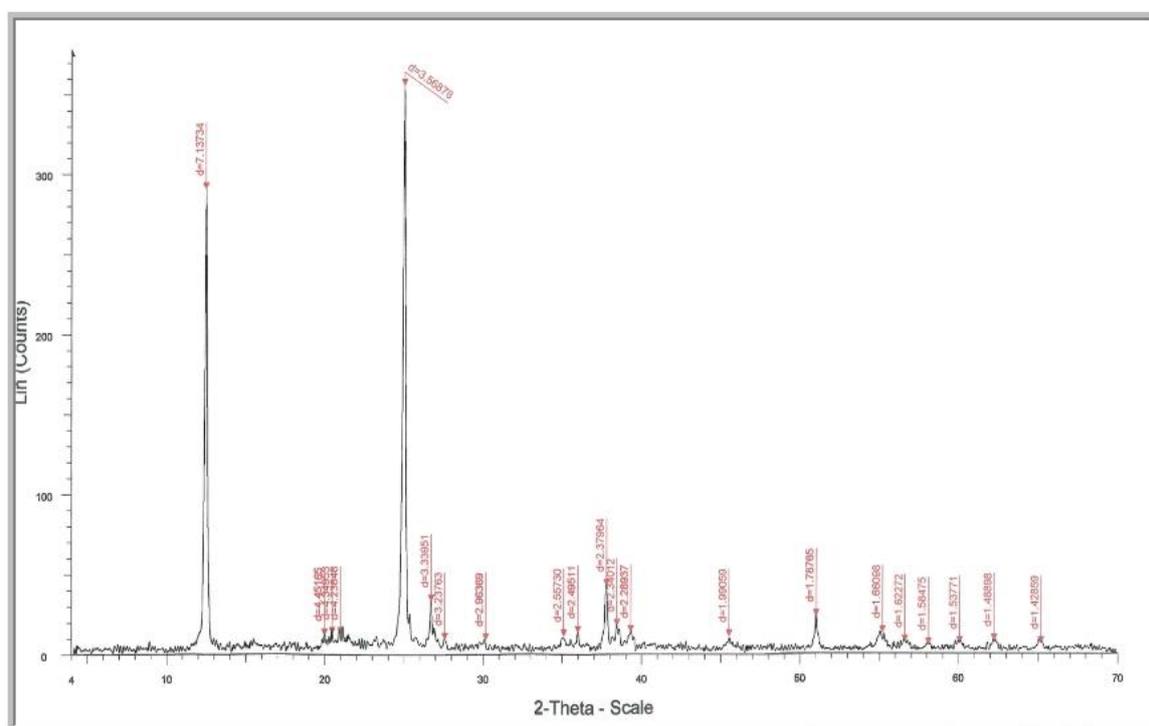
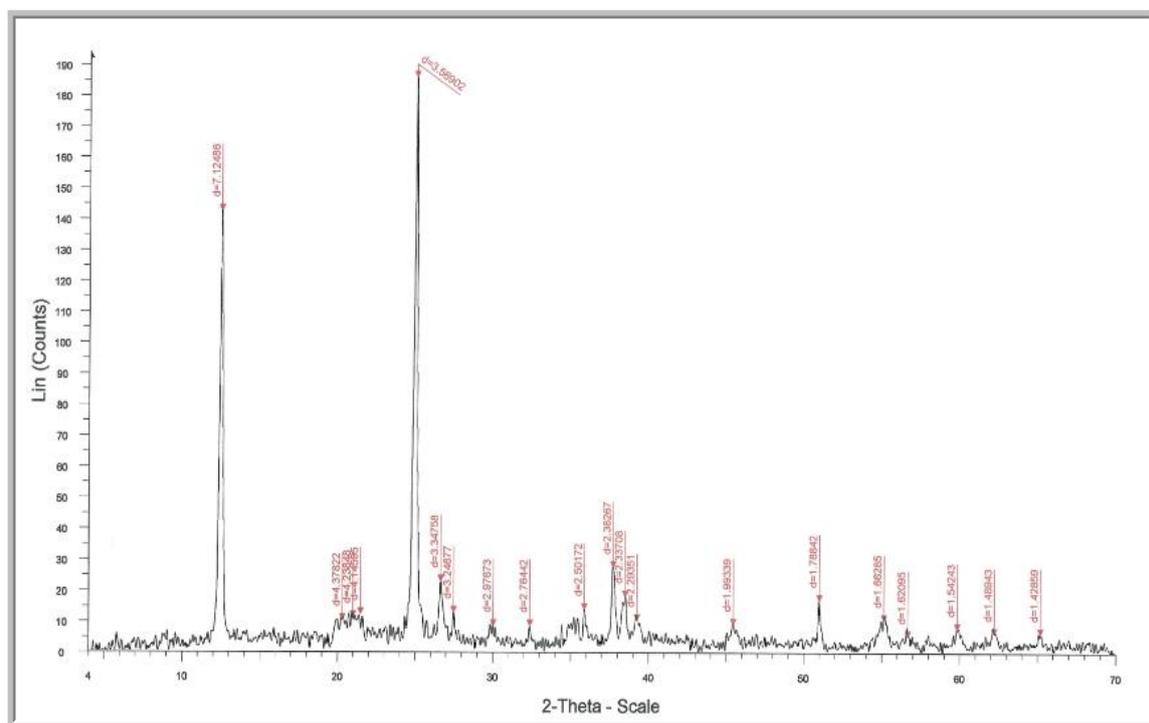


Figure (11) X-Ray diffraction pattern of 70%kaolinite/ 30%PMMA nanocomposite



**Figure (12)** X-Ray diffraction patterns of 60%kaolinite/ 40%PMMA nanocomposite

X-ray diffraction pattern of kaolinite, shown in figure (2), indicate that the d-spacing's of the kaolinite is equal to 0.715nm where the natural position is at about  $2\theta = 12.35^{\circ}$ .

The treatment of the kaolinite, in one hand, to increase the basal spacing in order to enhance intercalation of the polymer chains within the inter-platelet gallery and exfoliation of the clay platelets among the polymer matrix and, on the other hand, to compatibilize the surface of the kaolinite platelets with the polymer chains, facilitating thus the dispersion of the clay within the polymer matrix.

Figure (3) shows the evolution of the XRD (001) basal plane of the kaolinite as a function of the chemical treatment. It can be seen that the modification process results in further shift of the basal peak towards lower angles, which indicates that the clay interlayer distance increases as a result of the treatment.

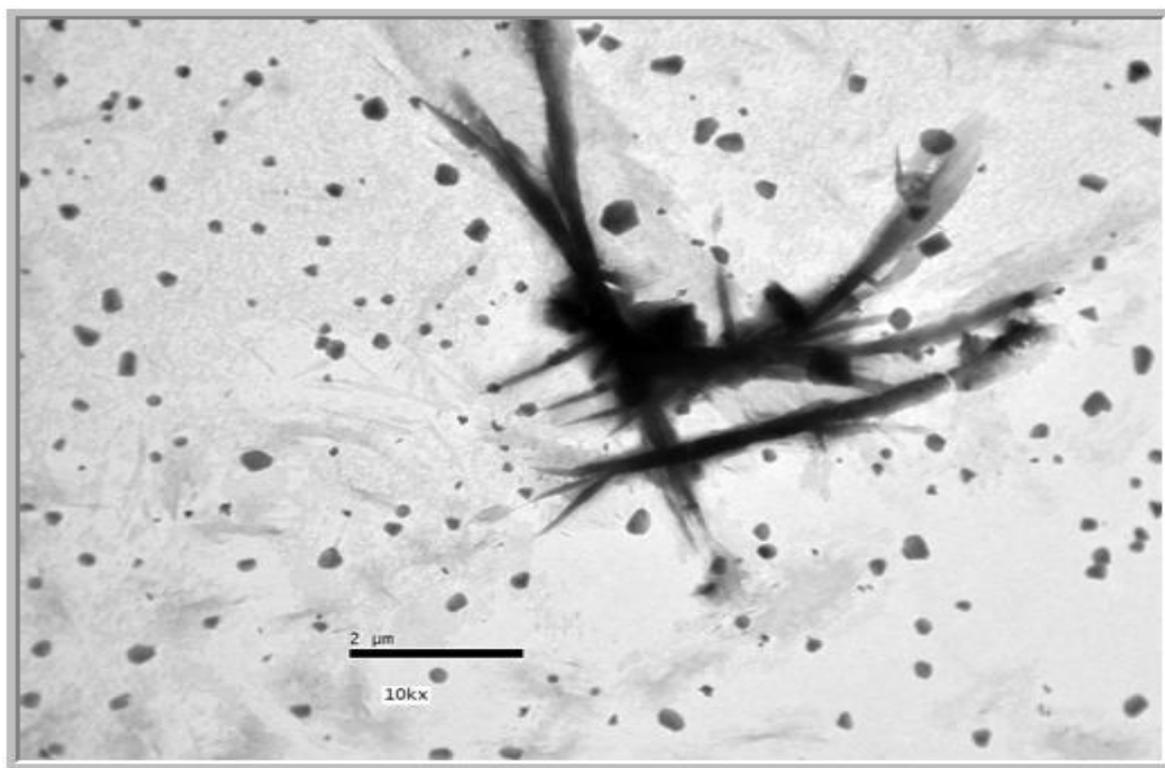
Table (2) lists the positions of the basal peak (001, corresponding d-spacing's of the unmodified kaolinite. Table (3) lists the positions of the basal peak (001), corresponding, d-spacing's of the same kaolinite after the modification process. From this table(3), it can be seen that the addition of DMSO leads to a shift of the basal peak of the kaolinite (001) from its natural position at  $2\theta = 12.35^{\circ}$  to  $2\theta = 7.88^{\circ}$ , which represents an increase in d-spacing from 0.715 to 1.12 nm, which is about 55%. This increase is thought to occur by absorption of highly polar DMSO molecules over the surface of the kaolinite platelets.

Figure (4) shows the data of the PMMA that was determined by X-ray diffraction. On the trace of PMMA in the range of  $2\theta = 4 - 60^{\circ}$ , a broad band centered at about 14 and  $30^{\circ}$  is occurred. The significance of this broad band is that it means PMMA is amorphous.

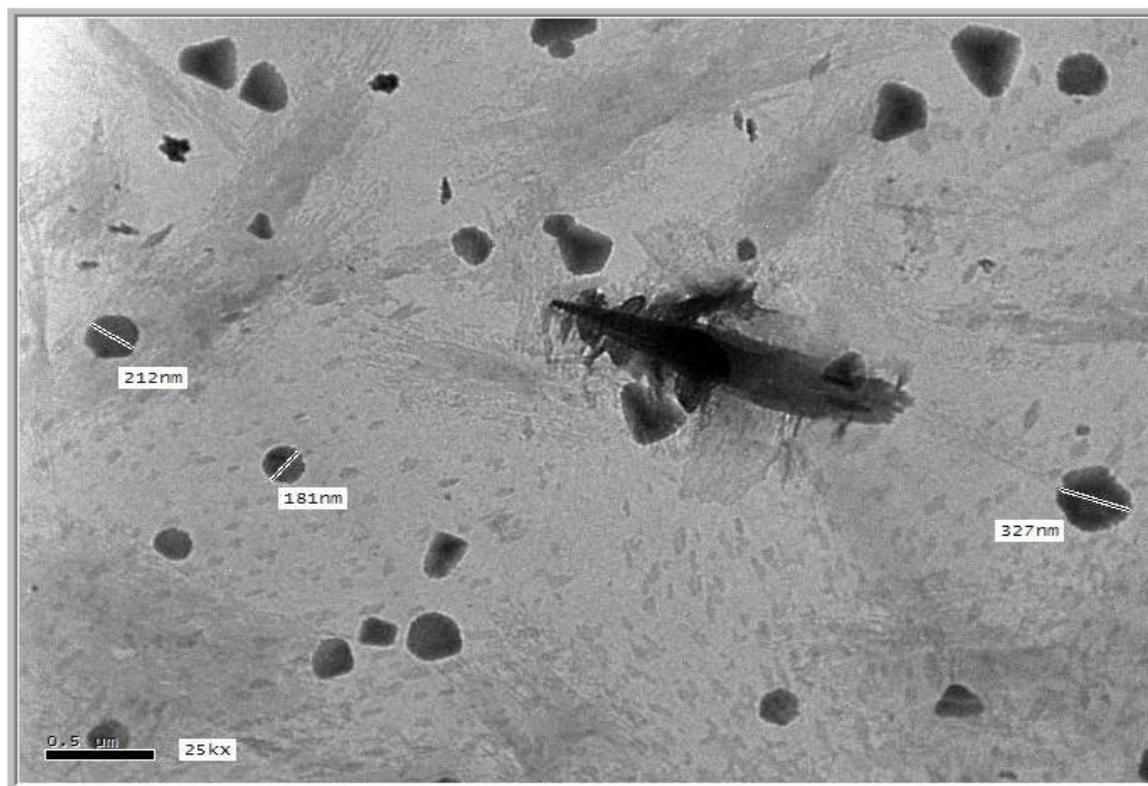
Figure (5) exhibits that the peak of  $d_{001} = 1.12$  nm is vanished, whereas the  $d_{001} = 0.72$  nm conserved, it is the peak of conserved kaolinite in kaolinite/DMSO. The result supports that kaolinite/DMSO was intercalated by PMMA successfully; also the broad bands in figures (6) to (8) support the conclusion that the intercalated kaolinite in the intercalation nanocomposite is a certain degree of crystallizability although intercalated clay exist. While it is impossible to synthesize PMMA/kaolinite intercalation composite with kaolinite under the same condition that appears clearly in figures (9-12) where the amorphous PMMA does not appear. Then the method of preparation of kaolinite/DMSO was effective for the compounding of kaolinite with PMMA.

### Transmission Electron Microscopy for samples

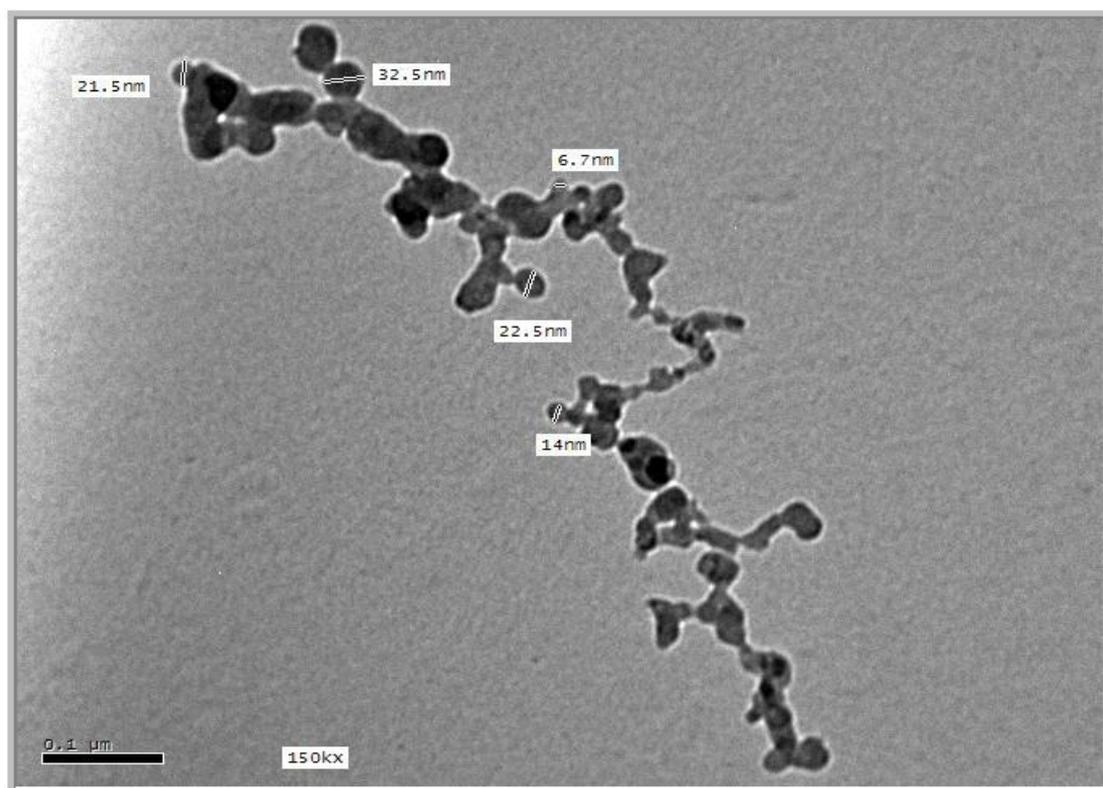
Transmission electron microscopy (TEM) for all samples was performed using a JEOL 1230 equipped with fully automated computer control. It was used to study the microstructure, and to measure the particle size for each sample. Figures (13) to (16) show the images of the samples resulted from TEM with a magnification between 10kx to 150kx.



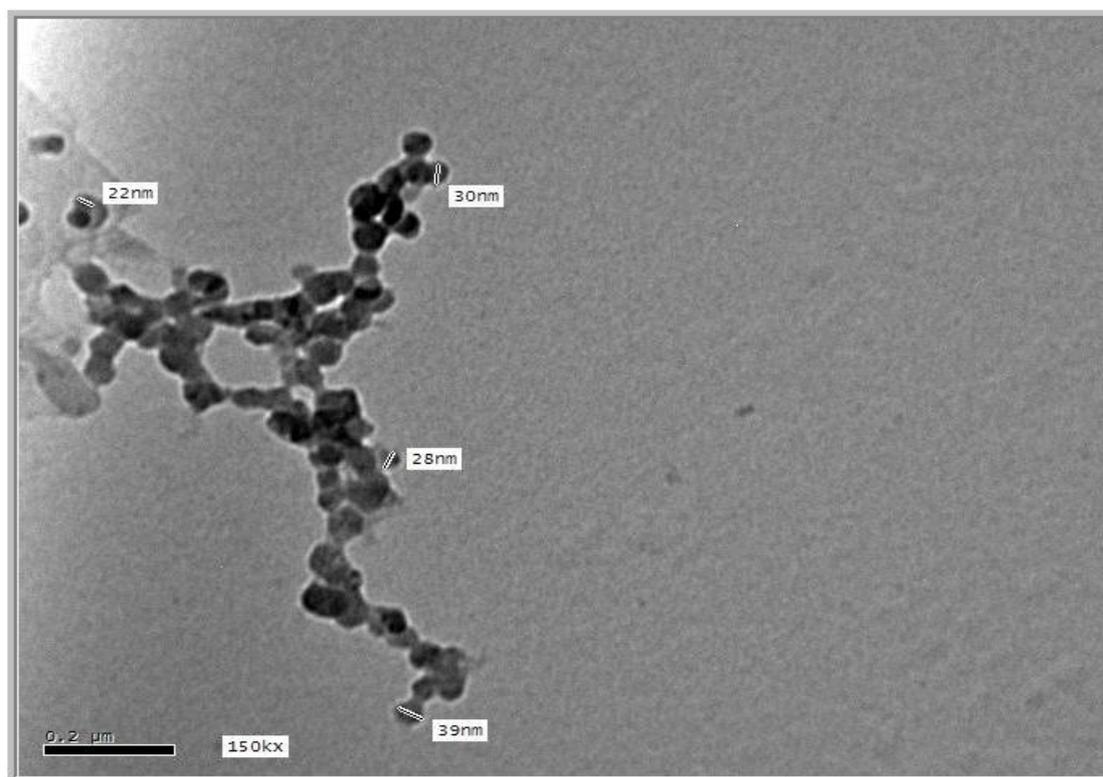
**Figure 13a** TEM image of natural kaolinite at magnification of 10kx.



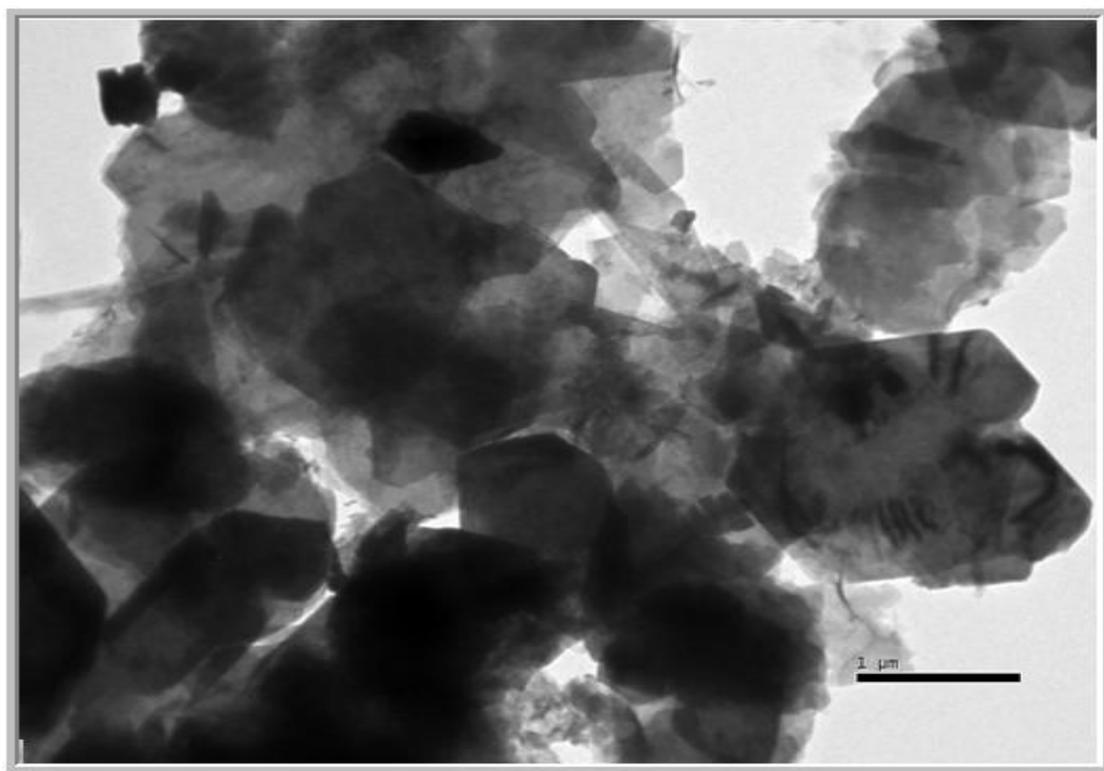
**Figure 13b** TEM image of natural kaolinite at magnification of 25kx.



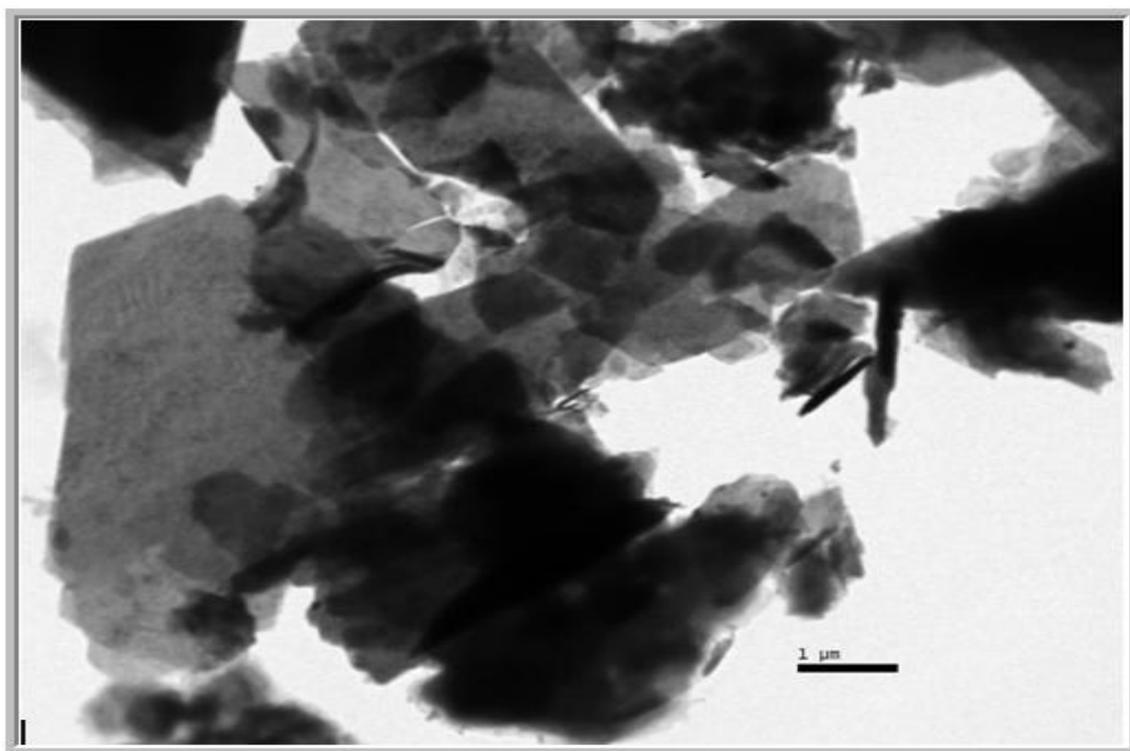
**Figure 14a** TEM image of kaolinite+DMSO at magnification of 150kx.



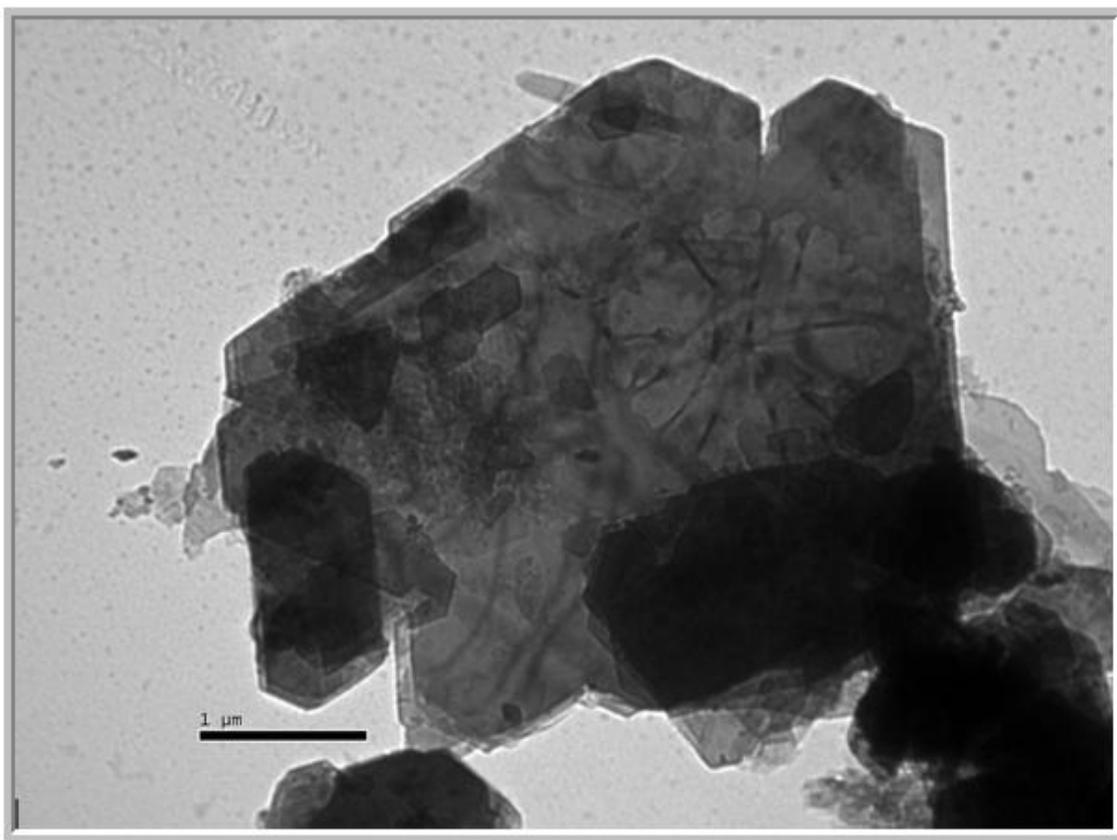
**Figure 14b** TEM image of kaolinite+DMSO at magnification of 150kx.



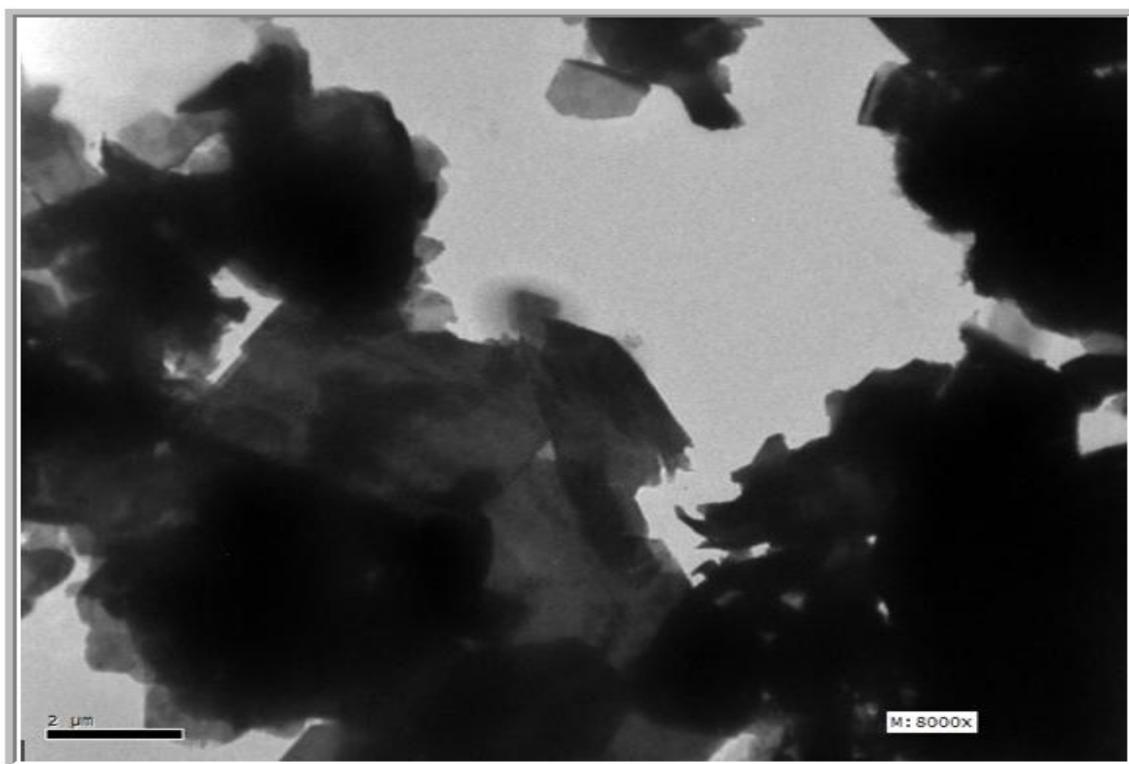
**Figure 15a** TEM image of (kaolinite+DMSO)/PMMA nanocomposite



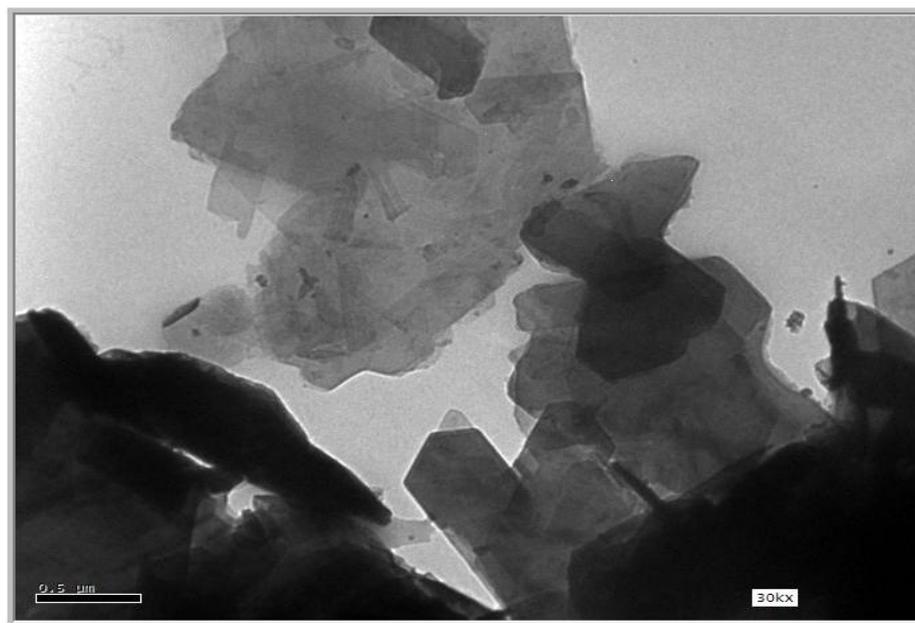
**Figure 15c** TEM image of (kaolinite/DMSO)/PMMA nanocomposite



**Figure 15c** TEM image of (kaolinite/DMSO)/PMMA nanocomposite



**Figure 16a** TEM image of kaolinite/PMMA nanocomposite



**Figure 16b** TEM image of kaolinite/PMMA nanocomposite

Figures (13, a, b) show different TEM images of kaolinite. In figures (14, a, b) the intercalation of DMSO in kaolinite can be clearly observed. (Kaolinite+DMSO)/PMMA nanocomposite shown clearly in figures (15, a, b, c.). TEM images of kaolinite/PMMA were shown in figures (16, a, b). The observations indicate that insufficient shear is achieved during the mixing step, which leads to a completely exfoliated morphology of kaolinite platelets by the polymer matrix. Another likely explanation is the removal of chemical modification elements from the kaolinite gallery, leading to a collapse of the clay morphology towards its natural state, making complete exfoliation difficult to be attained.

Thus, although there is kaolinite aggregation in the final microstructure of the nanocomposites, the size of these is in the nanometer range and their aspect ratio is high enough to expect significant property improvements.

#### **IV. Conclusion**

To increase the d-spacing of kaolinite to intercalate of PMMA in the kaolinite clay mineral is so impossible, until the kaolinite have been treated with a polar solvent (e.g.: DMSO). Let the kaolinite in a polar solvent in a sufficient time to achieve a good intercalation, and to get maximum basal spacing between the layers.

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