



## Characterization of Some Polymeric Composite Ion exchangers

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### Abstract

Polymeric composites were prepared by template polymerization process in aqueous solution. Thermogravimetric analysis (TGA), differential thermal analysis (DTA) and The X-ray diffraction patterns (XRD) were performed to evaluate the physico chemical properties of the different polymeric composite resins. The TGA and DTA clarify high thermal stability of the prepared polymeric composites. XRD of some the prepared polymeric composites show that there is crystalline structure while others are amorphous one.

**Key words: template polymerization, polymer composite, TGA, DTA, and XRD.**

### Introduction

A wide range of materials is available as ion exchangers. These materials have variety forms and widely different chemical and physical properties and can be naturally occurring or synthetic. Also they can be inorganic (mineral, oxides, etc) or organic (generally polymer) based. Composite ion exchangers consist of one or more ion exchangers combined with another material, which may be inorganic or organic and may be itself ion exchanger<sup>(1)</sup>. The reason for manufacturing a composite material is to overcome the limitation properties of organic resins (the mechanical strength, thermal and radiation stability) and inorganic adsorbents (fabrication for column applications)<sup>(2)</sup>. Composite resins can be prepared by adding of some inorganic adsorbents such as clay and its



minerals, zeolites, and hexacyanoferrate into organic materials such as polyacrylonitrile.

There are different methods for preparing of composite exchangers, such as copolymerizing, or grafting one. Template polymerization is a modern polymerization method that can be used in polymerizing of different monomers for preparing of polymeric composite resins. Template or matrix polymerization<sup>(3, 4)</sup> is defined as a polymerization in which chain propagation occurs along a preformed template, i.e. a polymer, added to the reaction system. Interpolymer complex is a product of template polymerization; the characteristics of these complexes, resulting from cooperative interactions differ from those of the constituent polymers<sup>(5)</sup>. The complexation is generally attributed to successive hydrogen bonding, hydrophobic interactions, ionic interactions or Van der Waals forces.

A polymer-metal complex is a coordination complex resulting from the reaction of a ligand function anchored on a macromolecular matrix with a metal ion. The structural environment of the ligand function is one of the key factors determining the complexing ability of polymeric ligands with metal ions. A ligand in a polymer is subjected to a multitude of structural environments in contrast to a low-molecular-weight ligand. Hence the physicochemical properties of the derived polymer-metal complexes also depend on the polymer support<sup>(6)</sup>. The nature of the polymer backbone, the degree of crosslinking, the coordination geometry of the metal centers and the ligand structure are decisive in affecting the thermal stabilities of polymer-metal complexes.

In this work TGA and DTA were used to estimate the thermal stability of polymeric composites such as poly(acrylamide-acrylic acid)-ethylenediamine tetra acetic acid disodium salt P(AM-AA)-EDTANa<sub>2</sub>,



poly(acrylamide-acrylic acid)-montmorillonite P(AM-AA)-montmorillonite, and poly(acrylamide-acrylic acid)-potassium nickel hexacyanoferrate P(AM-AA)-KNiHCF, also, crystallinity of the polymeric composites one studied using X- ray diffraction.

## **Experimental**

### **Preparation of polymeric composite:**

#### **Preparation of polyacrylamide:**

Polyacrylamide was prepared by a gamma radiation-initiated polymerization of acrylamide monomer in aqueous solution at a monomer concentration of 10% and a radiation dose of 10 kGy at a dose-rate of 10 kGy/hr<sup>(7)</sup>.

#### **Preparation of polymeric-EDTANa<sub>2</sub> composite:**

N,N'-methylene diacrylamide (DAM) aqueous solution (1%) was mixed with P (AM) gel (3%), then different concentrations of EDTANa<sub>2</sub> were mixed with this mixture. The mixture was stirred vigorously at a room temperature for about 2 hour. After that, AA (10% aqueous solution) was added. Finally, the solution was irradiated at a present temperature and a dose of 20 kGy. After irradiation solidified samples were cut into small pieces after precipitation in acetone, then dried and analyzed.

#### **Preparation of polymer montmorillonite composite resin:**

The sample preparation procedure was as follows. DAM aqueous solution (1%) was mixed with P (AM) gel (3%), and then the different concentrations of montmorillonite were mixed with this mixture. The mixture was stirred vigorously at room temperature for about 2 hour. After that, AA (10% aqueous solution) was added. Finally, the solution was irradiated at the present temperature and a dose of 20



kGy. After irradiation the solidified samples were cut into small pieces after precipitation in acetone, dried and analyzed.

### **Preparation of polymeric-hexacyanoferrate composites:**

P (AM-AA) - KNiHCF prepared by the following procedure:  
DAM aqueous solution (1%) was mixed with P (AM) gel (3%), and then different concentration of potassium nickel hexacyanoferrate (KNiHCF) gel was mixed with this mixture. The mixture was stirred vigorously at room temperature for about 2 hour. After that, AA (10% aqueous solution) was added. Finally, the solution was irradiated at present temperature and dose of 20 kGy.

### **Preparation of potassium nickel hexacyanoferrate (KNiHCF)**

KNiHCF was prepared according to the procedure reported by Remes<sup>(8)</sup>. A known volume of solution containing 100 g l<sup>-1</sup> of nickel(II) chloride was added to an equal volume of a solution containing 100 g l<sup>-1</sup> of potassium hexacyanoferrate(III), 100 g l<sup>-1</sup> of potassium hexacyanoferrate(II) and 15 g l<sup>-1</sup> potassium phosphate and mixed vigorously. The obtained (KNiHCF) precipitate was washed by distilled water.

### **Characterization**

Polymeric composites obtained by template polymerization were washed several times with distilled water and dried under vacuum. In order to complete remove of water, the samples were dried at 90 °C for 30 min before characterization by DTA, TGA, and XRD.

### **Thermal analysis:**

Thermal analysis (DTA, TGA) was under taken using simultaneous DTA-TGA a shimadzu thermogravimetric analyzer model DTG-60H.



### **X-ray diffractometer**

Shimadzu XD-DI X-ray diffractometer was used to study the diffraction behavior of polymeric composites. All the experiments were carried out between  $2\theta$  equal to  $4^{\circ}$  to  $70^{\circ}$ . Thin film samples of average thickness equal to 400-500 microns were used. Experiments were carried out at room temperature. The basal spacing or the  $d$  spacing was calculated by using Bragg's equation:

$n \lambda = 2d \sin \theta$ , Where,  $\lambda$ = wavelength,  $d$ = interplanar distance, and  $\theta$ = diffraction angle

## **Results and Discussions**

### **Thermal decomposition behavior**

Thermogravimetric analysis may be considered the most particular widely used method to illustrate the thermal stability of polymer over a wide range of temperatures. Thermogravimetry (TG) measures the change in the weight loss of sample as a function of temperature. The weight loss takes place as a result of degradation of original samples and also secondary reaction of initial degradation products. The thermal stability of polymeric materials depends on many factors, such as bond strength, activation energies, crosslinking, melting or softening, the presence of low molecular weight volatile(or impurities) and weak links, and the presence of groups which are readily modified by heat etc<sup>(9)</sup>.

In the present work, TGA was used to investigate the thermal stability of some polymeric composites. Also, the thermal stability of the



latter composites was studied after interaction with Cu (II) (after cation build- up).

The initial TGA thermograms for P (AM-AA)-EDTANa<sub>2</sub> and P (AM-AA)-EDTANa<sub>2</sub>-Cu are shown in Figs. (1, 2). It can be seen that these polymeric composites of P (AM-AA)-EDTANa<sub>2</sub> and P(AM-AA)-EDTANa<sub>2</sub>-Cu after approximately 250 to 290<sup>0</sup>C undergo thermal decomposition. Further thermal decomposition is occurred between 300 and 400 <sup>0</sup>C. Table (1), shows the weight loss percentage at different decomposition temperatures for both P(AM-AA)-EDTANa<sub>2</sub> and P(AM-AA)-EDTANa<sub>2</sub>-Cu.

From the data of Table (1), the weight loss of P(AM-AA)-EDTANa<sub>2</sub> and P(AM-AA)- EDTANa<sub>2</sub>-Cu is mainly divided into two parts. The first part from 1.6 to 3 % at 100 <sup>0</sup>C while at 200 <sup>0</sup>C the weight loss is approximately 8 %. As reported by McNeill et al. <sup>(10,11)</sup>, the first degradation process is related mainly to the loss of adsorbed or coordinated water molecules through the formation of intra- and intermolecular anhydride links and also to decomposition of uncoordinated amide and the carboxyl groups. This decomposition was carried out through the cyclization process with the removal of ammonia or water molecules from two amide groups or carboxylic groups respectively as shown in Figs.(3, 4). In the second degradation stage, the weight loss is about from 35 to 50 % at 300 <sup>0</sup>C while at 400 <sup>0</sup>C the weight loss is approximately from 50 to 65%. The loss in weight in this part is related to the polymer decomposition with the elimination of CO and CO<sub>2</sub>



due to abundant backbone scission and formation of a small unsaturated species.

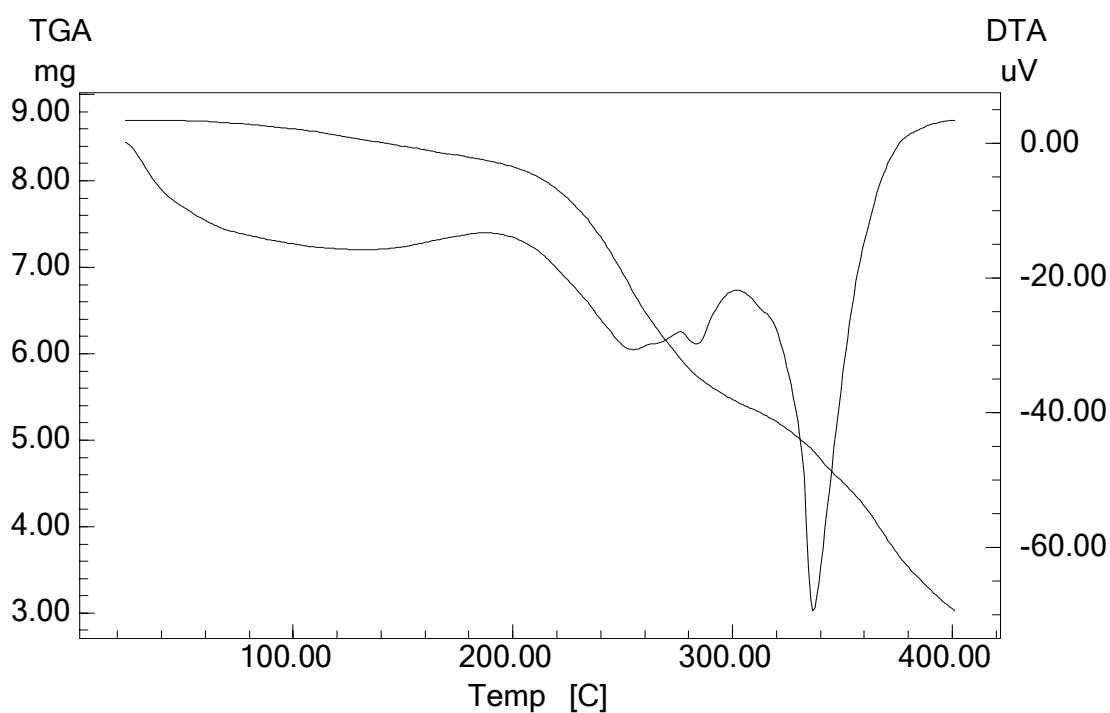


Fig.(1):DTA and TGA curve of P(AM-AA)-EDTANa<sub>2</sub>

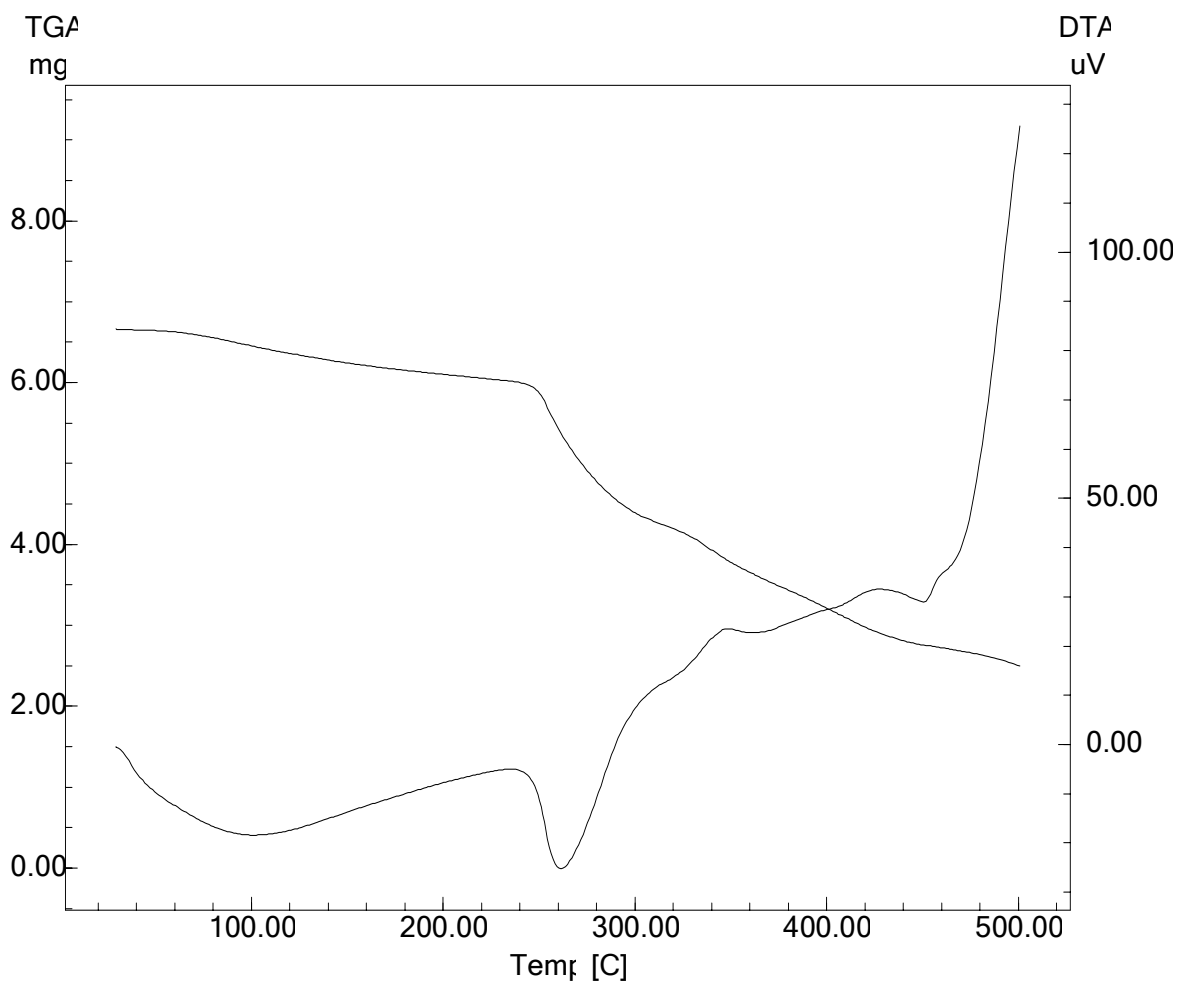


Fig.(2):DTA and TGA curve of P(AM-AA)-EDTANa<sub>2</sub>-Cu

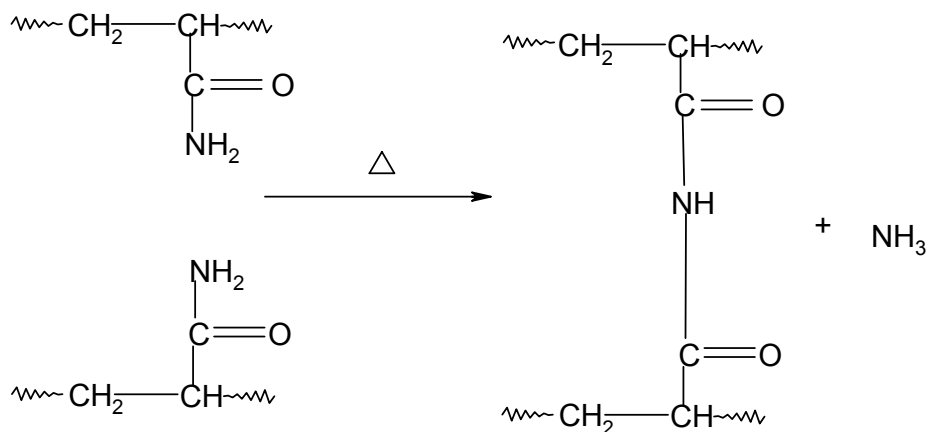
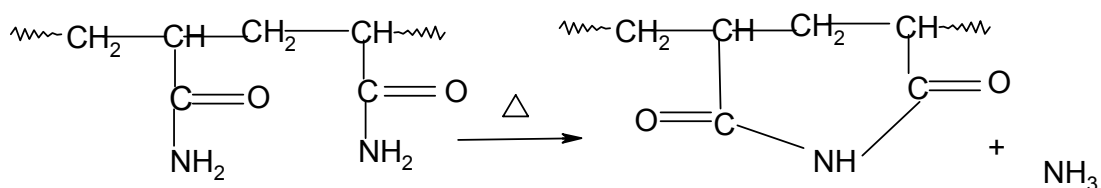
**Table (1) weight loss of polymeric composites at different decomposition temperatures.**

Polymeric composites	Weight loss(%) at decomposition temperature(°C)				
	100	200	300	400	500
P(AM-AA)-EDTANa <sub>2</sub>	1.6	8.7	52.9	64.6	
P(AM-AA)- EDTANa <sub>2</sub> -Cu	3.2	8.5	34	51.8	62.4

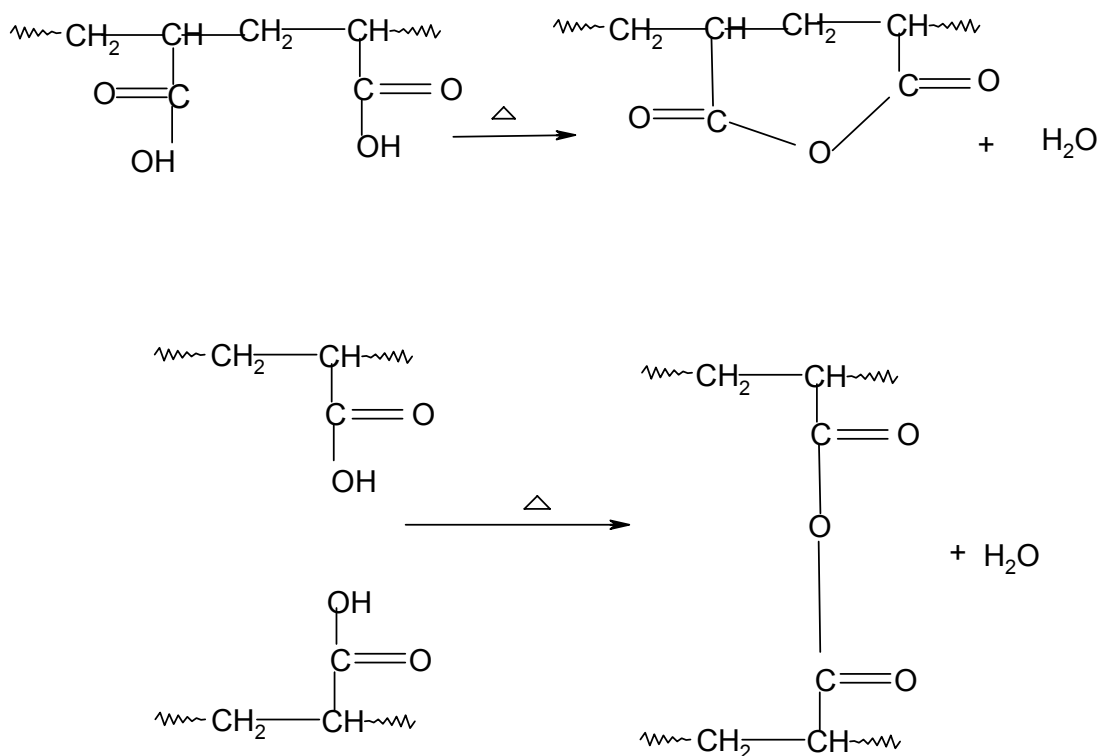




P(AM-AA)–montmorillonite	0.9	2.29	12.4	18.3	
P(AM-AA)–montmorillonite-Cu	6	13.8	46.5	70	94
P(AM-AA)-KNiHCF	3.12	8.6	16.8	19.7	27
P(AM-AA)-KNiHCF-Cu	1.6	5.5	7.7	9.5	12



Figure(3) Structure of imidation of P(AM) by heat.



Figure(4) Structure of decarboxylation of P(AA) by heat.

From the data of Table(1), it can be observed that, the thermal stability of P(AM-AA)- EDTANa<sub>2</sub>-Cu is higher than that of P(AM-AA)- EDTANa<sub>2</sub>; this could be due to the incorporation of the metal-ion on the polymer depends on the nature of the bond formed between the polymer functional groups and the metal ion. Such bond has usually ionic and covalent character. Ionic bond rearranges the polymeric chains more really than the covalent bond, so the metal-ion stabilizes the polymer by increasing the degree of crosslinking between the polymeric chains, hence the liberation of ammonia will be decreases so the cyclization of amide groups inhibited. The Cu(II) interact with -COONa of (EDTANa<sub>2</sub>) groups through ion exchange mechanism, this leads to formation of sex member ring , consequently the thermal stability increases<sup>(7)</sup>.



The thermal behavior of P(AM-AA)-montmorillonite and P(AM-AA)-montmorillonite-Cu are shown in Figs.(5,6). It can be seen that the polymer-montmorillonite start to decompose at about 260 to 290<sup>0</sup>C. The TGA thermograms of P(AM-AA)-montmorillonite and P(AM-AA)-montmorillonite-Cu are summarized in Table(1). The data in thermograms and Table (1), show two degradation stages. In the temperature region from room temperature to 200<sup>0</sup>C the weight loss assigned to the elimination of water molecules adsorbed to the hydrophilic polymer. The probable structure of polymer- montmorillonite is shown in Fig.(7)<sup>(12)</sup>. According to the experimental results, there should be absorbed water on the clay sheet surface, and also the water structure should exist in the clay sheets with the hydrogen bond <sup>(13)</sup>. At high temperature some water molecules are liberated by the reaction of hydroxyl groups in the clay sheet and polymer <sup>(13)</sup>. After increasing in temperature the bond breakage in the organic compound may occur outside the clay sheets, between C and N or C and O bonds.

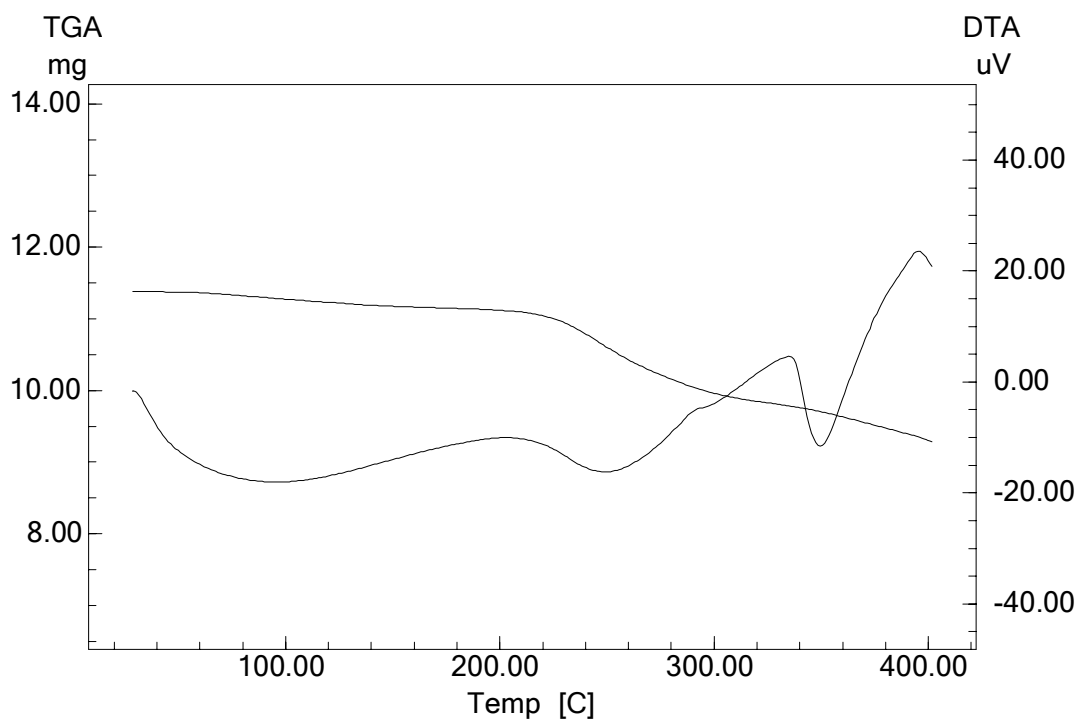


Fig.(5):DTA and TGA curve of P(AM-AA)-montmorillonite

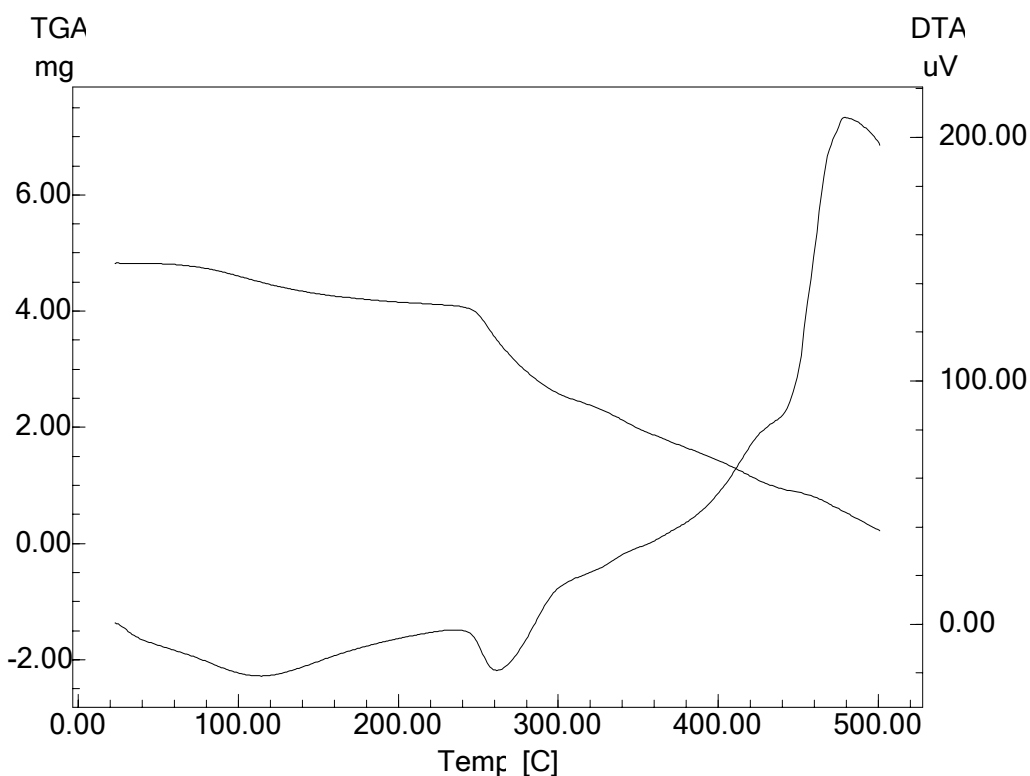
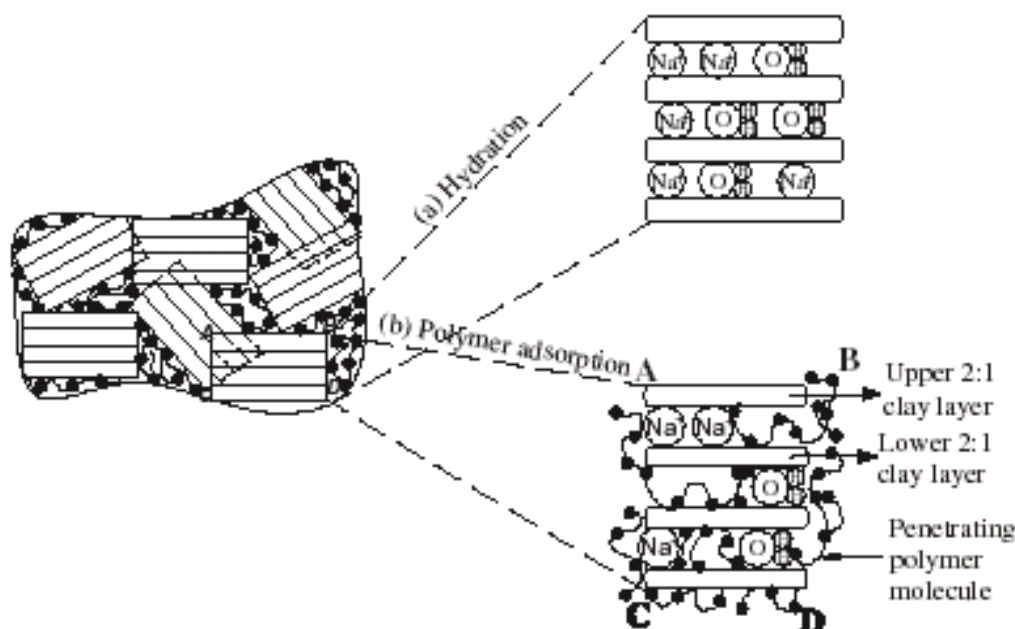


Fig.(6): DTA and TGA curve of P(AM-AA)-montmorillonite-Cu

Because there is less hindrance in the clay sheets, can evolve quietly without further degradation. At higher temperature, the organic compounds in the clay sheets decompose and the force correlate them, evolve slowly and further decomposition occurs mainly between C and C bonds. It is concluded that, the intercalated organic compounds decompose at higher temperatures, and the decomposition reaction are more complete than that outside organic compounds. This finding may be due to the interference between organic compounds and clay sheets<sup>(14)</sup>.



**Fig.(7). Schematic diagram of clay unit arrangement for (a) hydration and (b) polymer adsorption.**

From Table(1), it could be observed that the thermal stability of P(AM-AA)-montmorillonite is higher than that of P(AM-AA)-montmorillonite-Cu; this may be due to the Cu(II) enhance the thermal conductivity<sup>(9)</sup> of polymeric composites, consequently less energy will be required for the decomposition of the investigated resins.



The TGA curves of P(AM-AA)-KNiHCF and its Cu(II) complexes are shown in Figs.(8,9). It is shown that these polymeric composites start to decompose at about 250<sup>0</sup>C. The TGA thermogram of P(AM-AA)-KNiHCF and their Cu(II) complexes are summarized in Table(1).

The weight loss of P(AM-AA)-KNiHCF, and P(AM-AA)-KNiHCF-Cu are mainly divided into two parts. The first part from 1.6 to 3 % at 100<sup>0</sup>C while at 200<sup>0</sup>C the weight loss is approximately 5.5 to 8.5 %; this may be due to loss of water molecules adsorbed on the polymeric parts through coordination bonds also decomposition of uncoordinated amide and carboxylic groups as discussed above. With increasing temperature the weight loss increases, the weight loss is from 7.5 to 16% at 300<sup>0</sup>C, at 400<sup>0</sup>C the weight loss is approximately from 9 to 20% while at higher temperatures the losses in weight is about 12 to 27% . As discussed above the loss in weight in this part is related to the polymer decomposition with the elimination of CO and CO<sub>2</sub> by way of abundant backbone scission and formation of a small unsaturated species. The hexacyanoferrate part shows weight losses during heating due to losses water of hydration followed by losses of CN groups or oxidation, depending on the atmosphere<sup>(15)</sup>.

The data of Table (1), clarify that, the thermal stability of P(AM-AA)-KNiHCF-Cu is higher than that of P(AM-AA)-KNiHCF. This can be explained as discussed above in case of P(AM-AA)-EDTANa<sub>2</sub>-Cu and P(AM-AA)-EDTANa<sub>2</sub>, where the Cu(II) enhance the thermal stability thought the formation of linkage between polymeric matrix. This leads to the imidation and decarboxylation of amide and carboxylic groups respectively, will be decreases and hence the thermal stability will be increases.

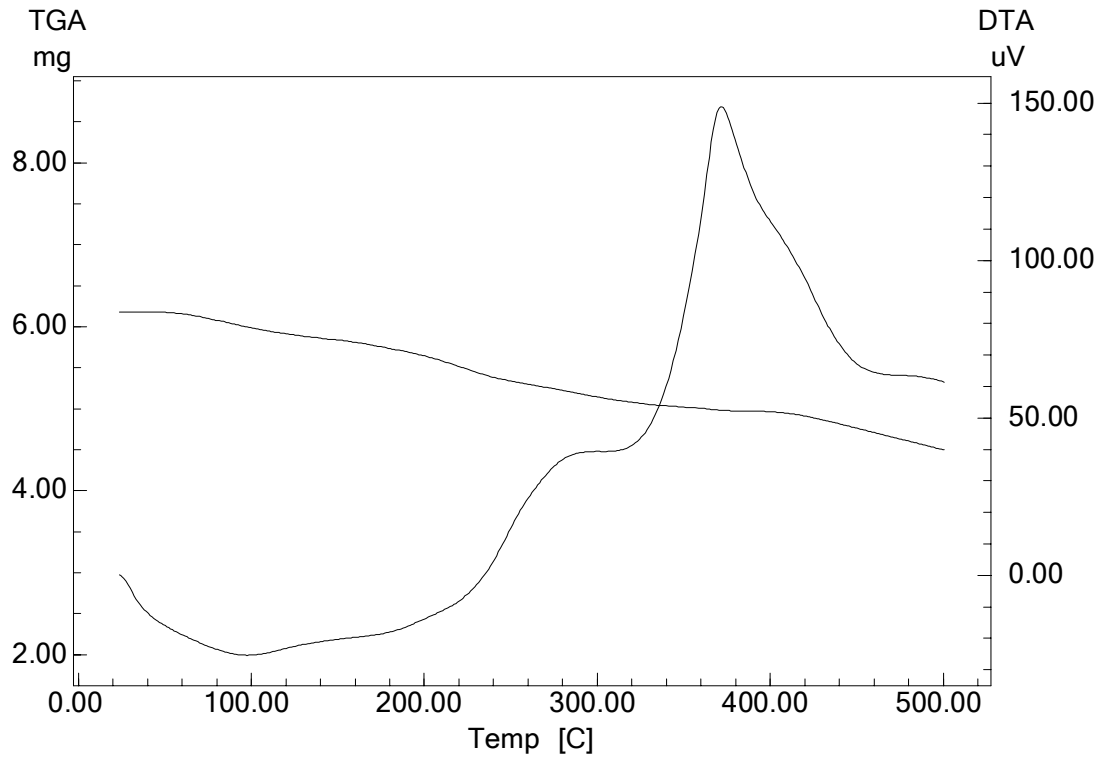


Fig.(8):DTA and TGA curve of P(AM-AA)-KNiHCF

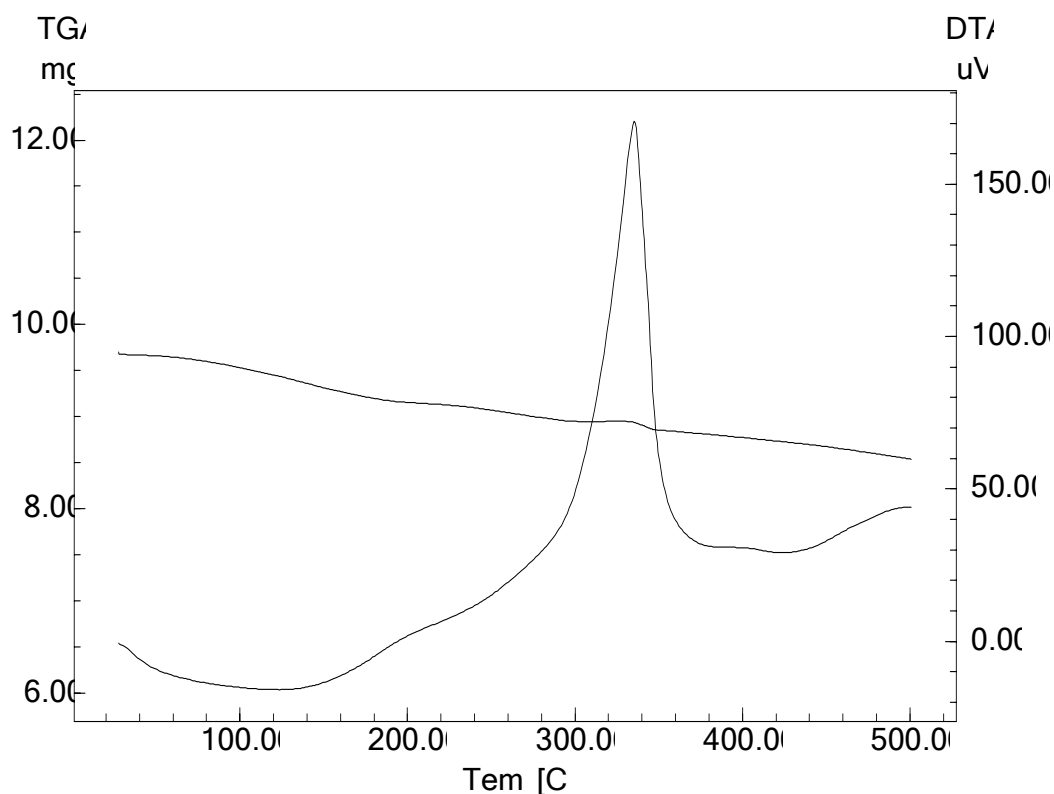


Fig.(9):DTA and TGA curve of P(AM-AA)-KNiHCF-Cu

Generally the incorporation of inorganic hexacyanoferrate part with organic part during preparation for production of polymeric composites increase the thermal stability when compared with the polymeric part alone, as mentioned by Kim et al.,<sup>(2)</sup>.

TGA data of Table (1), shows that, the thermal stability of the composites has the following order: P(AM-AA)-EDTANa<sub>2</sub>, P(AM-AA)-montmorillonite, and P(AM-AA)-KNiHCF. The thermal stability of P(AM-AA)-montmorillonite is higher than that of other polymeric composites which means that the intercalation of acrylamide and other chemicals into the interlayer of montmorillonite form thermally stable structure. This may provide a wide usage of the composite materials in relatively high temperature application fields<sup>(14)</sup>.





### Differential thermal analysis (DTA)

The measurements of DTA were carried out in nitrogen atmosphere. Where DTA was used to study phase transformation during heat treatment and can give accurate data about thermal stability of polymeric composites. The data obtained from DTA can be used to discuss thermal events such as onset temperature, endset temperature, peak temperature and enthalpy change ( $\Delta H$ ). The obtained data of DTA are shown in Figs.(1, 2, 5, 6, 8, 9).

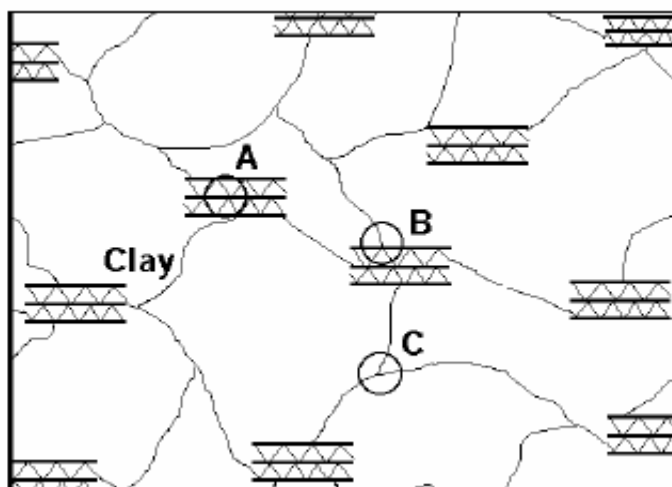
DTA of P(AM-AA)-EDTANa<sub>2</sub> and P(AM-AA)-EDTANa<sub>2</sub>-Cu data show that, there are three endothermic peaks appears for P(AM-AA)-EDTANa<sub>2</sub>. Two endothermic peaks are with maximum value at 255 and 336 °C may be related to its polymeric decomposition. It is well known that P(AM-AA)-EDTANa<sub>2</sub> formed by complexation (template polymerization) of P(AM) and P(AA) by hydrogen bonding, covalent bonding, and coordination bond through DAM and EDTANa<sub>2</sub>. It well known that P(AA) on heating don't become thermoplastic but crosslinked one. Chars, and decomposes<sup>(16)</sup>, and polyacrylamide is thermally more stable polymer and its degradation starts at 200 °C<sup>(17)</sup> through two steps. The first step from 200 to 340 °C corresponds to the loss of ammonia and water by imidization and dehydration, respectively. The second process, at temperature higher than 340 °C, is attributed to processes accompanying main chain scission. Consequently, the result endothermic peaks may be attributed to evaporation resulted on charring of P(AA) and degradation of P(AM). P(AM-AA)-EDTANa<sub>2</sub> have an endothermic at low maximum value (100°C) may attributed to loss of free water molecules adsorbed on polymer composites.

DTA curves of P(AM-AA)-montmorillinite and P(AM-AA)-montmorillinite-Cu show that there are three distinct endothermic peaks



one lower than 100<sup>0</sup>C and, between 200<sup>0</sup>C and 250<sup>0</sup>C(maximum:249), and between 320<sup>0</sup>C and 360<sup>0</sup>C(maximum:349). The first endothermic peak is related to elimination of adsorbed water molecules on surface. The second endothermic peak is a broad peak that consists of at least three endothermic peaks. Gaussian-Loventzian suggests that this peak results from combination of different peaks with maxima at 259<sup>0</sup>C, 282<sup>0</sup>C, 310<sup>0</sup>C and 329<sup>0</sup>C. These individual peaks may be related to the possible types of bonding. Since it is well known that the polymer intercalated with the montmorillonite through three state, the first one maybe attributed to intercalation of polymer chains into interlays of montmorillonite, and the second state resulted from interaction of polymer composite with surface of montmorillonite, while the third one may be related to the formation of free polymer network structure as shown in Fig.(10)<sup>(14)</sup>.

The coordinated surface water molecules at A, B and C-Sites will have different binding energies. Theoretically water associated with C-Sites (free polymer) should have lowest binding energy. Consequently, the first (and second) peaks at 259<sup>0</sup>C and 282<sup>0</sup>C may be related to water absorbed by the 'free' polymer, the third peak at 310<sup>0</sup>C may be related to water absorbed by PAM situated at B-sites, and the fourth peak at approximately 329 °C may be related to water absorbed by polymer intercalated in the interlayer space of the montmorillonite (A-sites)<sup>(14)</sup>.



**Fig.(10):**Schematic structure of a polymer/ montmorillonite composite. A-site: Polymer intercalated into the lamina of montmorillonite, B-site: Polymer attached to the surface of montmorillonite particles, C-site: Free polymer network.<sup>(14)</sup>

DTA of P(AM-AA)-hexacyanoferrate and P(AM-AA)-hexacyanoferrate-Cu system shows sharp exothermic peak due to thermal decomposition as the results of the liberation of ammonia molecules from the two adjacent of amide groups, also the presence of inorganic part of hexacyanoferrate leads to loss of -CN groups and formation of some oxides at high temperature<sup>(15)</sup>.

### **X-ray diffraction of the prepared polymeric composites.**

X-ray diffraction data gives a great deal of information about the quantitative aspects of disordered in crystal structure. Polymer crystal consists of perfect geometrical arrangement. However, defects and distortion are present in crystals of all materials, and together with grosser



types of disorder, they play an important role in the crystal structure of the polymers<sup>(19)</sup>.

X-ray diffraction patterns recorded for each of the polymeric composites of P(AM-AA)-EDTANa<sub>2</sub>, and P(AM-AA)-EDTANa<sub>2</sub>-Cu are given in Figs.(11,12), which show that two resins are fully amorphous. This may be due to the prepared polymeric composites have large side groups such as EDTANa<sub>2</sub><sup>(18)</sup>. Also, interaction of Cu (II) with polymeric chains increase the crosslinking, hence the amorphous structure are formed.

XRD patterns of P(AM-AA)-montmorillonite free or complexed with Cu(II) are shown in Figs.(13,14), it was performed to obtain quantitative information about the interring of polymer or monomers molecules into interlayer of clay mineral(montmorillonite)<sup>(12)</sup>. From Figs.(13,14), it is found that the P(AM-AA)-montmorillonite free or complexed with metal ions are amorphous(i.e. have no peaks). Strong interaction between montmorillonite and monomers or polymeric chains during synthesis takes place and leads to the absence of diffraction peaks corresponding to the interlayer basal spacing indicative of the distribution of ordered platelet separation leading to an exfoliated dispersion<sup>(19)</sup> as shown in Fig.(15).



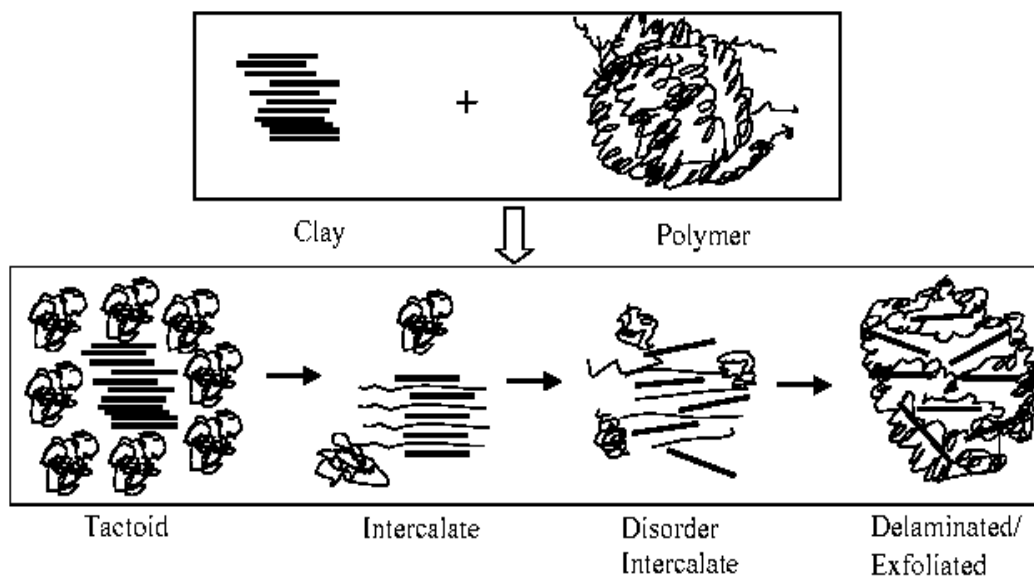
Fig.(11):X-ray diffraction patterns of P(AM-AA)-EDTANa<sub>2</sub>

Fig.(12):X-ray diffraction patterns of P(AM-AA)-EDTANa<sub>2</sub>-Cu



Fig.(13):X-ray diffraction patterns of P(AM-AA)-montmorillonite.

Fig.(14):X-ray diffraction patterns of P(AM-AA)-montmorillonite-Cu.



Figure(15) Different types of polymer clay composite

X-ray diffraction patterns recorded for P(AM-AA)-KNiHCF free or complexed with Cu ion are presented in Figs.(16,17). Which show that, the presence of some characteristic signals at different diffracting angles for free and complexed resins. This finding confirms the presence of crystal structure for them. The ( $dA^{\circ}$ ) values and relative intensities ( $I/I_0$ ) of XRD patterns for P(AM-AA)-KNiHCF and their copper complexes are given in Table(2).

It is clearly that the three peaks appeared with slight variations in the intensity and the peaks position. It could be referred that the presence of metal ions complexed with polymeric composites enhances their crystalline structure through formation of network structure.



Fig.(16):X-ray diffraction patterns of P(AM-AA)-KNiHCF

Fig.(17):X-ray diffraction patterns of P(AM-AA)-KNiHCF-Cu





**Table(2):X-ray diffraction data for P(AM-AA)-KNiHCF metal free and its copper complexes**

P(AM-AA)-KNiHCF		P(AM-AA)-KNiHCF-Cu	
dA°	I/I <sub>0</sub>	dA°	I/I <sub>0</sub>
3.6	100	5	100
3	99	3.55	95
5	97	2.5	77

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