

Preparation and characterization of Bentonite-Melamine and Bentonite-Bentonite-Melamineformaldehydepolymer complexes and study the physical molecular interactions of these systems

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Abstract

In this study the interaction between Iraqi Bentonite clay and Melamine was estimated by using FT-IR and XRD methods these methods indicate the Melamine molecule form interlayer complex with Bentonite unit crystal sheets through Hydrogen bonding and electrostatic forces this interaction increase the space dimension among clay sheets, the obtained complex was used to prepare the second complex by reaction with formaldehyde. The XRD pattern and FT-IR spectra show that the formation of the polymer was happen inside the space among clay sheets and the formatted polymer cause an irreversible change in the crystal structure of Bentonite that form the complex with polymer.

Introduction

In recent years polymer clay complexes have attracted great interest, both in industry and in academy, because they often exhibit remarkable improvement in materials properties when compared with virgin polymer or conventional micro and macro-composites. These improvements can include high module [1, 9], increased strength and heat resistance [10], decreased gas permeability [11, 12] and flammability [13, 14], and increased biodegradability of biodegradable polymers [15]. On the other hand, there has been considerable interest in theory and simulations addressing the preparation and properties of these materials [16, 17], and they are also considered to be unique model systems to study the structure and dynamics of polymers in confined environments [18, 19]. Although the intercalation chemistry of polymers when mixed with

appropriately modified layered silicate and synthetic layered silicates has long been known [20, 21], the field of these systems nano-composites has gained momentum recently. Two major findings have stimulated the revival of interest in these materials: first, the report from the Toyota research group of a Nylon-6 (N6) Bentonite nano-composite [22], for which very small amounts of layered silicate loadings resulted in pronounced improvements of thermal and mechanical properties; and second, the observation by Vaia et al. [23] that it is possible to melt-mix polymers with layered silicates, without the use of organic solvents. Today, efforts are being conducted globally, using almost all types of polymer matrices.

The major constituent of Bentonite clay is Bentonite mineral Bentonite is a naturally occurring 2:1 phyllosilicate, which has the same layered and crystalline structure as talc and mica but a different layer charge. [24, 25] The Bentonite crystal lattice consists of 1-nm thin layers, with a central octahedral sheet of alumina fused between two external silica tetrahedral sheets (in such a way that the oxygens from the octahedral sheet also belong to the silica tetrahedra). Isomorphous substitution within the layers (for example, Al^{+3} replaced by Mg^{+2} or Fe^{+2}) generates a negative charges defined through the *charge exchange capacity* (CEC). For Bentonite is typically 0.9-1.2 mequiv/g depending on the mineral origin [26]. These layers organize themselves in a parallel fashion to form stacks with a regular Van der Waals gap between them, called *interlayer* or *gallery*. In their pristine form their excess negative charge is balanced by cations (Na^+ , Li^+ , Ca^{+2}) which exist hydrated in the interlayer sheets [27]. The aim of this study is modifying Iraqi Bentonite clay with Melamine and Melamine formaldehyde polymer and observing its crystallographic changes in addition to the nature of interaction type between the Monomer and polymer with the clay.

Experimental

i) Materials and instruments.

Bentonite was obtained from Iraqi Company of Mining and Geological scanning, Melamine, Formalin, Hydrochloric acid were analytical grade from BDH. FT-IR spectra were done using SHIMADZU, FT-IR-8400s. FOURIER TRANSFORM also XRD patterns were done by SHIMADZU XRD-6000-general-purpose X-ray Diffractometer with CuK α (wavelength = 0.154 nm).

ii) Preparation of Complexes.

The Bentonite was washed with dilute HCl (1%) for activation then filtered and washed several times with deionized water to remove the acid and soluble materials, then dried in the oven at 100°C for 3 hours., the obtained Bentonite was blended and put in closed containers. Complex Bentonite-Melamine was prepared by mixing 25g from the clay with 5g of Melamine by using ceramic mortar with addition few drops of water to the mixture to complete the interaction, the mixing process was continued for 30 minutes, then the resulted mixture was left for one week in a closed flask to complete the diffusion process, the polymer was prepared by addition 6ml of formalin with last prepared complex using mortar and addition of drops of 2ml of HCl the mixing process was continued for half hour then put in water bath for two hours to complete the cross linking between Melamine Formaldehyde polymer chains.

Results and discussion

Figures (1), (2) and (3) indicate X-ray patterns of Iraqi Bentonite (B), Bentonite-Melamine complex (BM) and Bentonite Melamine Formaldehyde complex (BMF), in figure (1) the Bands between 5 to 10° at 2θ axis that analogous to d value between 16-8Å⁰ belongs to (001) plane [28] this plane is the major plane in Bentonite mineral the broadness of this band due to different moisture content of the clay sample[25], the second interesting band on the 2θ axis is 19.91° corresponds to d value 4.46Å⁰ this band belong to (003) plane [28] the last major characteristic band is 2θ=27°, d=3.35Å⁰ belongs to (005) plane which has the highest intensity of this mineral the band at 2θ=29.43°, d=3.03Å⁰ belongs to the same plane(005) but with different moisture content crystal[29], the secondary bands that characteristic of Bentonite are band at 2θ=20.85°, d=4.26Å⁰ belong to the reflection from (110) plane also there are two weak bands at 2θ=34.81°, d=2.58Å⁰ and 2θ=36.55°, d=2.46Å⁰ these bands belong to (130) and (120) planes[29]. Figure(2) that shows X-ray diffraction pattern of MB complex show number of interesting features the, first one is a decrease of the intensity of the band between 16-8Å⁰ which belong to the plane (001) this indicate the change of the dimension of the plane (001) and increase of d value of this plane, the new d value is larger than 18Å⁰ that require 2θ value below 5° this is out of scale of the instrument this supported by appearance of third order major reflection at 2θ=17.66°, d=5.02Å⁰ of the plane (003) while the band at 2θ=19.84°, d=4.47Å⁰ still belong to this plane but for clay crystals that did not form a complex with Melamine the decrease of the strength of the

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minor band $2\Theta=34.81^\circ, d=2.58\text{\AA}$ of (110) plane and the appearance of the bands $2\Theta=20.75^\circ, d=4.28\text{\AA}$ and $2\Theta=22.03^\circ, d=4.03\text{\AA}$ represent the change of the length and width of the crystal unit those represented by the plane (110) also there is splitting in the band $2\Theta=26.57^\circ, d=3.35\text{\AA}$ and $2\Theta=29.35^\circ, d=3.04\text{\AA}$ which belongs to the major plane (005) and appearing of the bands $2\Theta=26.13^\circ, d=3.4\text{\AA}$ and $2\Theta=28.75^\circ, d=3.1\text{\AA}$ for the same reason which is the increase height of the major axis for number of Bentonite crystals and remaining a number of them unchanged these data indicate the Melamine molecules are interred the space between clay layers of some of its crystals that made them large change of the height of the crystal value and slight change to its length and width. Figure (3) that belong to the X-ray diffraction pattern of BMF complex show continues decrease of the peak heights but this time as a reason of increasing amorphousness of the sample due to the formation interlayer complex of poly Melamine Formaldehyde complex with Bentonite the characteristic peaks of the un-complexed clay crystals are returned to the original state but those that interred the complexation with polymer are disappeared and indicating the disappearance of the crystal structure of the complex and forming amorphous material that composed from the polymer and clay constituents. Figure(4) show FT-IR spectra for the Bentonite moderate bands at 3630cm^{-1} and 3421cm^{-1} belongs to stretching vibration of hydroxyl group at different environments [30] the broadness in this band is due to hydrogen bonding formation with interlayer water molecules the bending vibration band of water molecule is 1649cm^{-1} [31] the strong band at 1037cm^{-1} belong to the asymmetric vibration of the unit [Si-O-Si(Al)] [32] while its symmetric vibration at 532cm^{-1} [32]. Figure (5) show FT-IR spectra of Melamine which indicate several bands above 3000cm^{-1} due to symmetric and asymmetric vibrations of NH_2 groups these bands originally must be 6 equal to the number of N-H bonds but these six vibrations are overlap with each other to produce two sharp bands at $3418, 3470\text{cm}^{-1}$ and two broad bands at $3131, 3333\text{cm}^{-1}$ [33], bands at $1651, 1550, 1462$ and 1435cm^{-1} belong to stretching vibration of C=N bonds[34]. Figure (6) is FT-IR spectra for complex B-M this figure shows decreasing OH frequency of Bentonite to 3628cm^{-1} and remaining the highest frequencies of N-H bond in Melamine unchanged which indicate the decrease of the strength of Bentonite OH group through the increasing of H-bonding among Bentonite OH groups and Melamine molecules in a way that Bentonite be the donor of the proton while Melamine molecules be the acceptor also the H-bonding among Melamine molecules are decreased by the formation the H-bonding complex with Bentonite this clear from the increasing the frequencies of the broad band of N-H bond that caused by protonation of one NH_2 group in the Melamine molecule

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to 3345 and 3134cm^{-1} , in addition the bands that belong to C=N vibration frequencies all of them show a blue shift as an indication to the increase of their strength by this H-bonding and formation of a plus charged Melamine molecule, the band of the structural Bentonite Si-O-Si(Al) at 1032cm^{-1} indicates weakness of this bond, this may be the result of interaction of the positively charged Melamine molecules with negatively charged aluminosilic groups of Bentonite. Figure (7) shows the formation of the interacted polymer with Bentonite, we observe the disappearance of Melamine NH_2 groups, a continuous decrease in Bentonite OH frequencies resulted from stronger H-bonding interaction with polymer N atoms, the bands between 1500 to 1600cm^{-1} that belong to C=N group indicate the increase in the variety of its types as a consequence of the formation of new types of this bond through the polymerization process. Also, the frequency of the Si-O-Si(Al) band decreased from the BM complex case and became more broad, this means the electrostatic interaction with polymer units became weaker and the broadness belongs to the variety of interaction.

Conclusion

The XRD and FT-IR measurements on the Iraqi Bentonite clay that was modified with Melamine indicate that the Melamine molecules form an interlayer complex with Bentonite crystal sheets through hydrogen bonding and electrostatic forces. This interaction increases the space dimension among clay sheets, when these Melamine molecules form a polymer, this growing polymer acts to alter the crystal structure of the clay. Those we expect from these results is the improvement of the Bentonite properties for industrial use such as fiber glass filler and pollution removing, and this will be a project for future studies.

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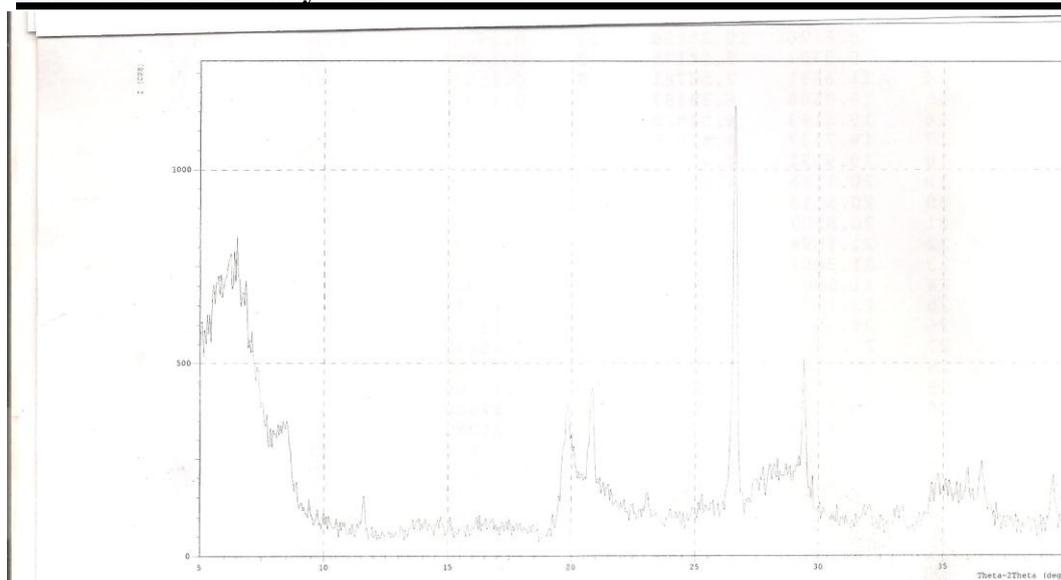


Figure (1) XRD pattern of Bentonite.

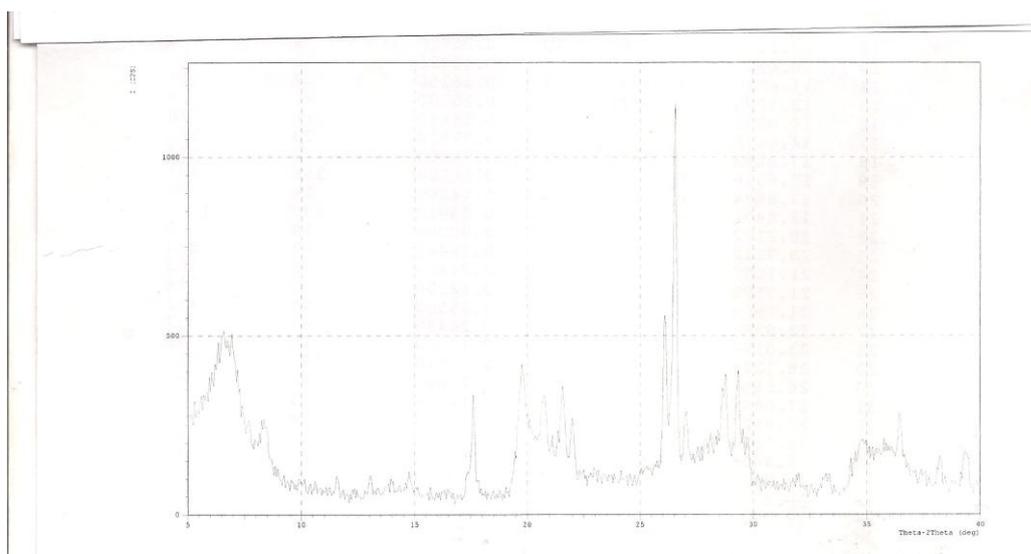


Figure (2) XRD pattern of Bentonite-Melamine BM complex.

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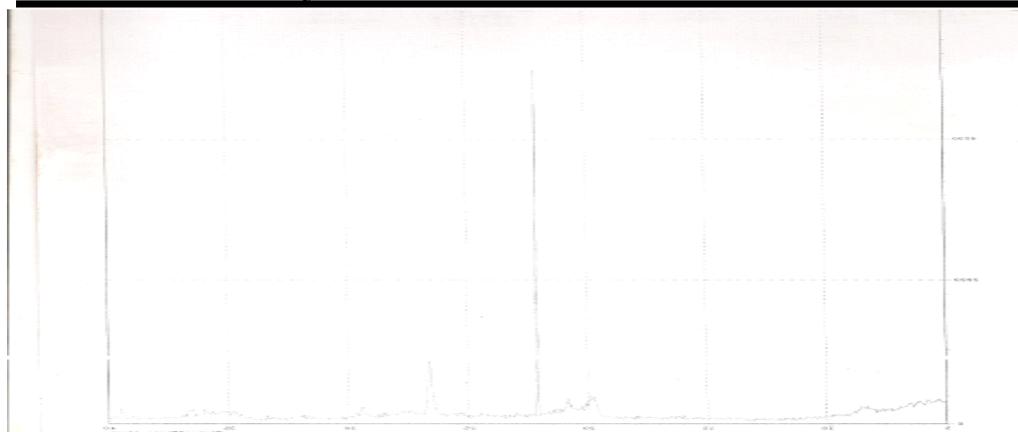


Figure (3) XRD pattern of Bentonite-Melamineformaldehyde polymer BMF complex.

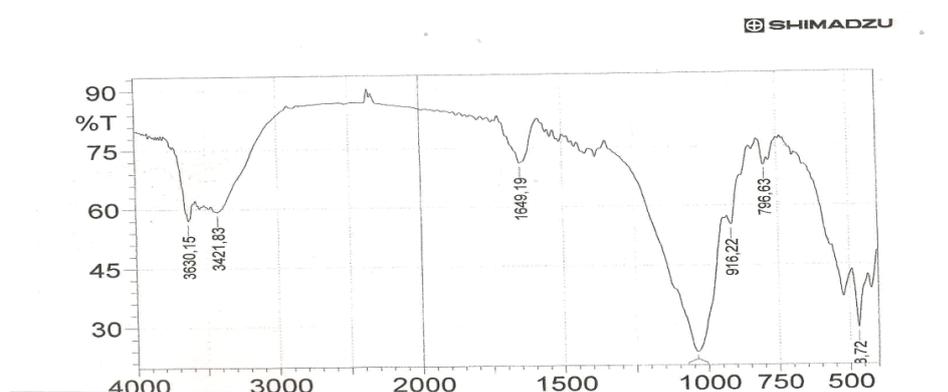


Figure (4) FT-IR spectra of Bentonite.

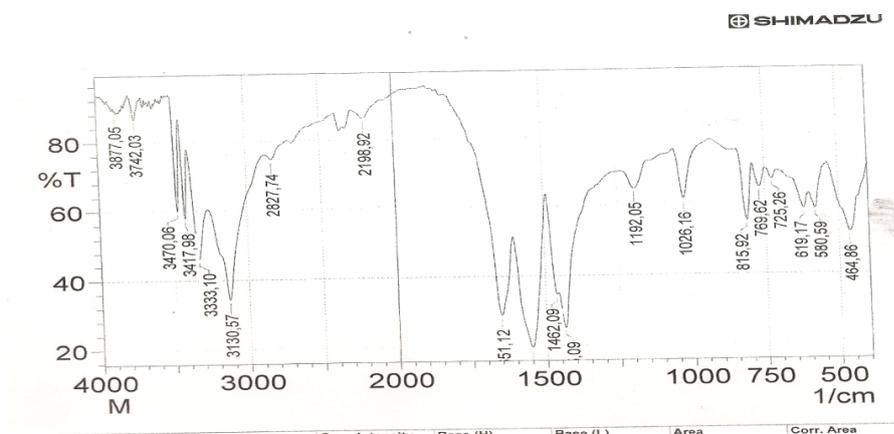


Figure (5) FT-IR spectra of Melamine.

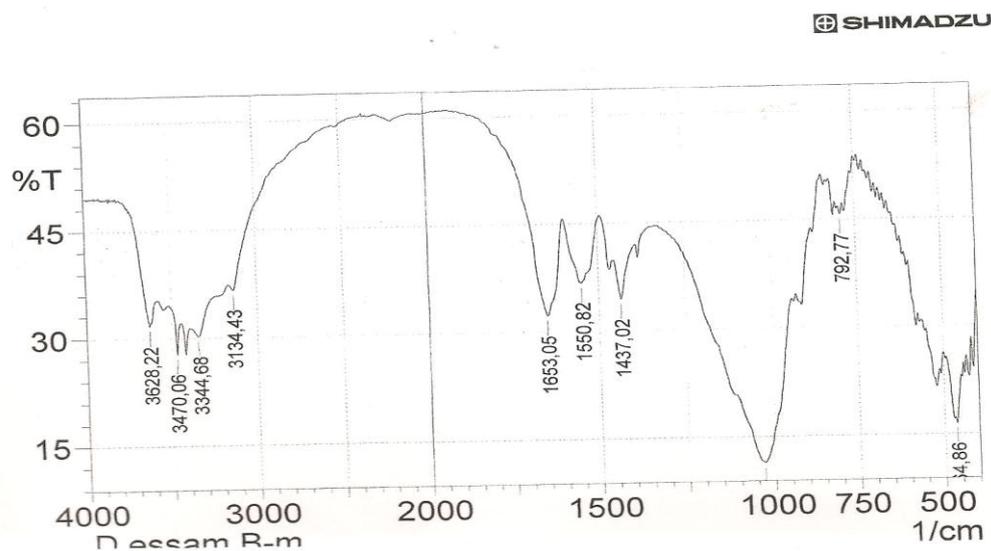


Figure (6) FT-IR spectra of Bentonite-Melamine BM complex.

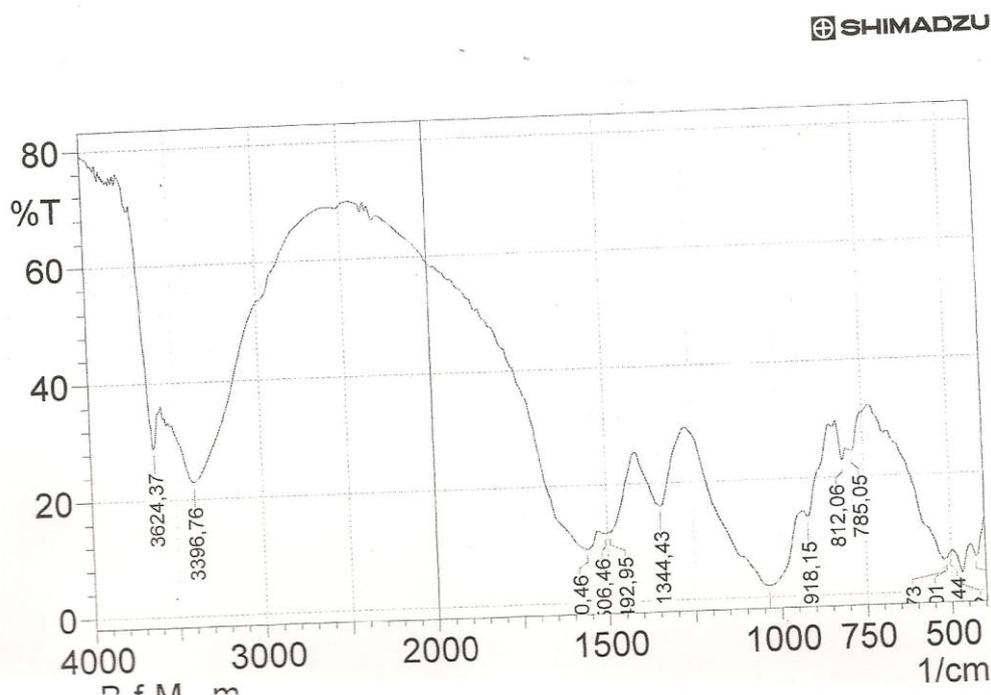


Figure (7) FT-IR spectra of Bentonite-Melamineformaldehyde polymer BMF complex.

تحضير و تشخيص معقدي البنتونايت-ميلامين و البنتونايت-ميلامين فورمالديهايد بوليمر و دراسة التداخلات الجزيئية الفيزيائية لهذه الانظمة.

الخلاصة

في هذه الدراسة تم تعيين التداخل الجزيئي بين طين البنتونايت العراقي مع الميلامين باستخدام تقنيتي FT-IR و XRD حيث بينت النتائج ان جزيئة الميلامين تدخل كمعقد بيني ضمن طبقات وحدة البلورة لمعدن البنتونايت من خلال قوى التاصر الهيدروجيني و التداخل الالكتروستاتيكي ,حيث يعمل هذا التداخل على زيادة المسافة بين طبقات معدن الطين ,استعمل المعقد الناتج لتحضير معقد البوليمر من خلال تفاعل الاول مع الفورمالديهايد و اظهرت بيانات FT-IR و XRD ان البوليمر كان قد تكون في الفضاءات بين طبقات معدن البنتونايت حيث سبب تكون البوليمر تغيرا لا رجوعي في التركيب البلوري للبنتونايت الذي كان قد كون معقدا مع الميلامين.