SYSTEM BASED ON CLAY/POLYMER FOR BIOMEDICAL APPLICATION

N. Belmessaoud Baa[1,*], N. Bouslah Mokhnachi [1] and N. Haddadine [1]

[1]University of Sciences and Technology Houari Boumediene. Faculty of Chemistry, Laboratoire de Synthèse Macromoléculaire et Thioorganique Macromoléculaire, El Alia, BP32, Bab Ezzouar, 16111, Algiers, Algeria

ABSTRACT

The objective of the present research was to investigate the intercalation of polymer-based surfactant, namely polyethylene-glycol (PEG) as a new montmorillonite MMT modifier inside the interlayer sheets of montmorillonite. A full microstructural characterization of the synthesized composites clays-polymers by XRD, FT-IR, TGA and DSC was performed. The XRD patterns and the FTIR spectra of the composites revealed that PEG was successfully intercalated into the galleries of MMT-Na since the basal spacing of the modified clay minerals was increased. The effect of the introduction of the clay on the crystallization temperature (Tc), melting temperature (Tm) and crystallization degree of PEG in the composites was prospected by DSC. The decrease of thermal stability of PEG in the nanocomposite, detected by TGA analysis is ascribed to the loss in the crystallinity of the PEG.

Keywords: PEG; nanocomposites; Clay; montmorillonite; intercalation.

1. INTRODUCTION

Nanoclays are a type of layered silicates with at least one dimension of the particle in the nanometer range which can be optimized for use in clay-based nanocomposites [1,2]. The most

commonly used type of layered silicate is montmorillonite (MMT) owing to its abundance, environmentally friendliness and well-studied chemistry. Being a member of the smectite group, with a 2:1 layer linkage, it has two tetrahedral sheets of silica sandwiching a central octahedral sheet of alumina. Its layers are stacked by weak dipolar or Van der Waals forces, and it has both surface and edge charges. The use of (MMT) clay as nanofiller for the preparation of polymer bio-nanocomposites still attract a lot of attention in both fundamental and applied research due to their outstanding mechanical, thermal, chemical molecular barrier, flame retardant, corrosion protection properties [3-8] and electrical properties over pure polymers [9,10]. These materials have many applications as they provide substantial properties enhancements, even at low nanoparticles content. The major problem in preparing nanocomposite materials based on MMT clay is the hydrophilicity of the clay that makes it less compatible with the organic polymers. To get a good dispersion and distribution of the filler, organic modification of the mobile surface cations, may facilitate the delamination of the clay layers into nanoscale platelets by the polymer chains. This is usually done by cationic exchange using surfactants having compatibility with the organic polymers such as alkylammonium or alkyphosphonium [11-12]. However, the use of organoclays containing cationic surfactants in biomedical applications should be limited since most of these quaternary ammoniums may be cytotoxic. The organic modification of MMT by using organic biopolymers instead of organic surfactant may be an effective method for compatibilizing the modified clay and the polymers for the elaboration of well defined nanocomposites.

Poly (ethylene glycol) (PEG) is a highly water soluble hydrophilic polymer and has wide range of applications in pharmaceutical industry [14]. The solubility of this polymer in water is due to the formation of H-bonding complexation between water molecules and polar group of the polymer molecules. In this study the preparation of polymer-modified MMT composites has been reported in order to use this hybrid as a drug delivery system. The effect of introducing MMT on the thermal properties and microstructure of PEG/MMTcomposites was investigated.

2. EXPERIMENTAL

2.1. Materials

Poly ethylene glycol of macromolecular weight Mw=10 000 were purchased from Fluka.

The clay used, MMT, is a natural montmorillonite from Mostaganem (Algeria) provided by the national non-ferrous mining products and valuable substances (ENOF Algeria).

The sodium montmorillonite MMT-Na was prepared in our laboratory.

2.2. Preparation methods

The montmorillonite was first purified [15]. The submicron fraction of the clay was separated by gravity sedimentation following Stokes law [16]. For this purpose, we conducted as a first step its purification with several portions of deionized water with vigorous stirring for 24 h to cause the delamination of the montmorillonite. In a second step we treated the purified MMT clay in an HCl acid solution (1N) in order to activate it. The third stage of the change was to standardize the existing cations in the interlayer space of montmorillonite, and the saturation of the clay with NaCl solution (0.5N). The clay recovered at the end of this step is a sodium montmorillonite; it is noted MMT-Na. Samples of MMT-Na/PEG were prepared according to solution cast method using deionized water as solvent. After stirring the PEG solution and the MMT-Na solution separately for 24 h, the mixture was introduced into an ultrasonic bath at a temperature of 60°C for 1h 30 min, after which it is casted onto plates.   The samples were first dried at room temperature to reduce the evaporation rate and to avoid film cracking. After evaporation of most of the solvent the samples were placed in a vacuum at 50°C.

2.3. Characterization

XRD patterns were recorded at 4°/min on a Phillips PW1710 diffractometer by using CuK radiation at a generator voltage of 50 kV and a generator current of 180 mA.

The FT-IR spectra of the samples were taken with a Perkin Elmer FT-IR C91566 Model FT-IR spectrophotometer using KBr pellets.

The thermogravimetric measurements were performed on a TAQ500 instrument under nitrogen atmosphere from room temperature to 700 °C at a heating rate of 10 °C/min.

DSC thermograms were carried out using a Perkin Elmer, DSC Diamond. Samples with weights between 5 and 10 mg were then sealed into an aluminium pan. An empty aluminium sealed pan was used as reference material. The temperature was raised from 25 to 180°C at a heating rate of 20°C/min under nitrogen atmosphere.

3. RESULTS AND DISCUSSION

3.1. X Ray Diffraction study (XRD)

XRD analysis was used to evaluate the intercalation of PEG into the interlayer space of the MMT-Na. The XRD patterns of PEG, MMT-Na and MMT-Na/PEG sample are shown in **Fig. 1**. Pure PEG exhibits typical reflections at 2 , 12.21°, 16.61°, 19, 0° and 22.3° [17]. The (001) reflection for pure MMT-Na was observed at 7.06 ° corresponding to a d-spacing of 12.51 Å [18]. This peak shifts to lower angles at 4.86° upon adding PEG suggesting that the d-spacing of MMT-Na increased to 18.16Å. The increased basal spacing after the reaction of PEG with MMT-Na is evidence of the intercalation of PEG into MMT-Na gallery and confirms the successful preparation of intercalated MMT-Na/PEG nanocomposites.
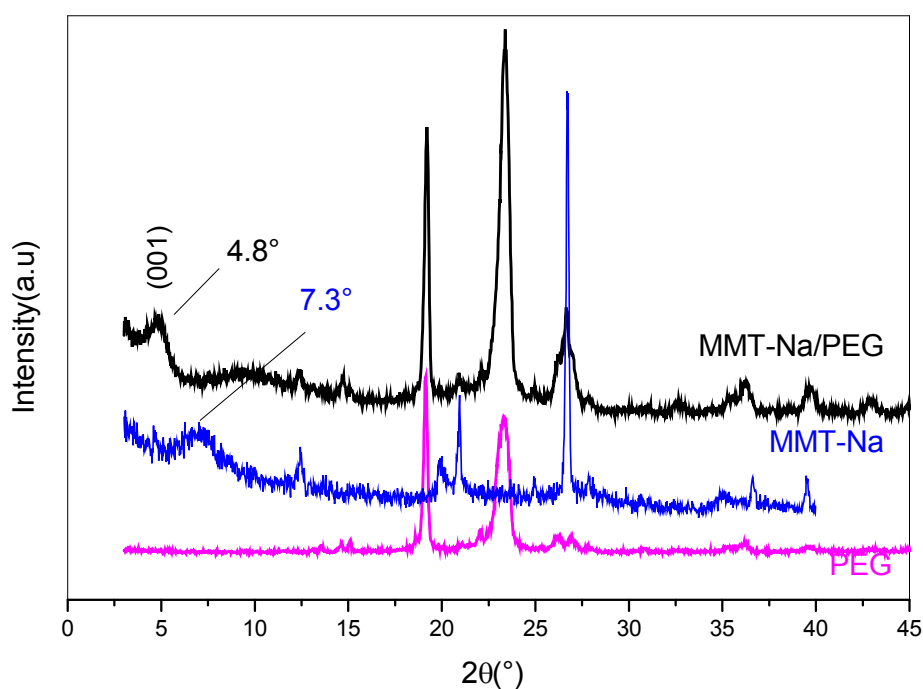
Fig.1. X-ray diffraction patterns of PEG, MMT-Na and MMT-Na/PEG nanocomposite.

3.2. Fourier Transform Infra-Red study (FTIR)

FTIR spectra of MMT-Na and MMT-Na/PEG are illustrated in Fig.2. In the FTIR MMT-Na spectrum, the broad band centered near 3446 cm^{-1} is due to the –OH stretching mode of interlayer water. The bands at 3621 and 3696 cm^{-1} are due to the –OH stretching mode of Al–OH and Si–OH of montmorillonite structure. The overlaid absorption peaks in the region of 1641 cm^{-1} is attributed to the –OH bending mode of absorbed water. The Si–O and Al–O

bonds are, respectively, observed at 1039 and 620 cm^{-1} and the Mg–O bond is assigned to the band at 530 cm^{-1} [19]. PEG spectrum shows characteristic bands of PEG such as the hydroxyl band at 3440 cm^{-1}, and C-H bands between 2950 and 2696 cm^{-1}. The bands at 1360 and 1344 cm^{-1} are assigned to CH$_2$ wagging modes; the bands at 1280 and 1234 cm^{-1} are associated with CH$_2$ twisting modes; the C-O-C stretching vibrations of PEG are well resolved to at least three bands at 1148, 1109 and 1061 cm^{-1}. The CH$_2$ rocking band of crystalline PEG occurs at 962 cm^{-1} [20]. All characteristic bands belonging to MMT-Na and PEG appear in the spectrum of MMT-Na/PEG especially the bands in the 3040-2877 cm^{-1} region corresponding to –C-H stretching of the PEG indicating the good insertion of the polymer in the MMT-Na galleries.
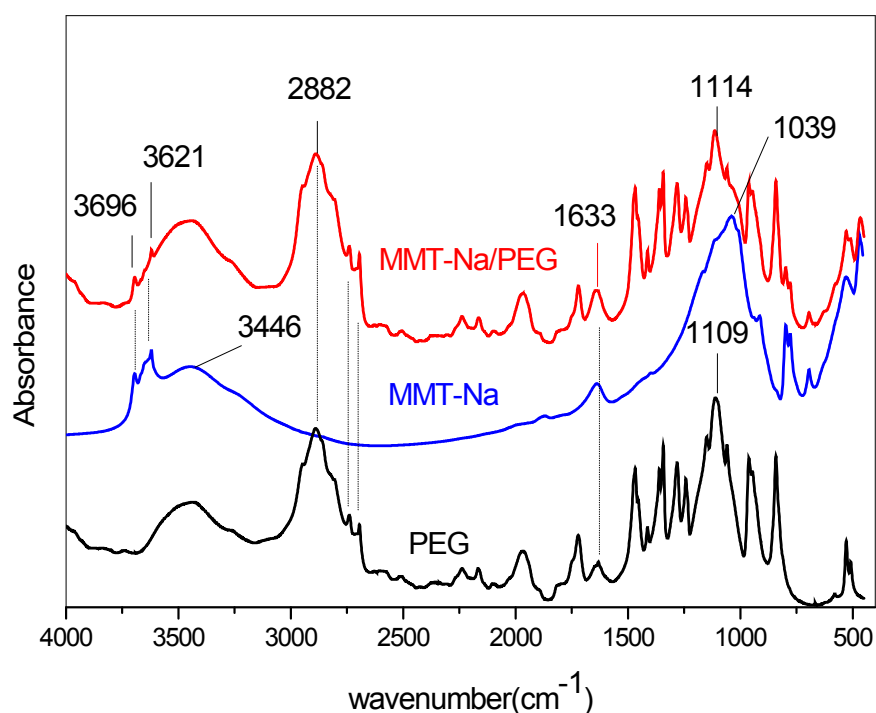

Fig.2. FT-IR spectra of MMT-Na, PEG and MMT-Na/PEG nanocomposite

Furthermore, the MMT-Na/PEG spectrum indicates that after PEG adsorbing on MMT-Na, the C-O-C stretching vibration appeared shifted to higher frequencies suggesting the development of interactions via hydrogen bonding between the oxygen of PEG and the hydroxyl groups at the surface of MMT-Na.

3.3. Differential scanning calorimetric study (DSC)

The DSC thermogram for pristine PEG, Fig.3 (a) recorded on heating shows an endotherm at 65 °C, which corresponds to its melting point. The melting endotherm has shifted slightly to lower temperatures, at 62 °C in MMT-Na/PEG composite suggesting a less-ordered structure of PEG in MMT-Na/PEG nanocomposite compared to its pure crystalline form. This phenomenon is attributed to the presence of specific interactions between the PEG chains and the hydroxyl groups at the surface of the clay. The DSC thermograms of pristine PEG and MMT-Na/PEG composites recorded up on cooling are illustrated in Fig.3 (b). PEG thermogram shows an exothermic peak which correspond to the crystallization temperature $T_C=32°C$.   The crystallization temperature MMT-Na/PEG composite was higher ssuggesting that the clay has acted as a nucleating agent. In this case, in the molten state, the segments of the PEG molecules can easily interact with the surface of MMT-Na, developing crystallization nuclei. This may be due to the high surface area of the Nano-sized particles that enhances heterogeneous crystallization. Similar results have been reported for nanocomposites by several authors [21- 23].
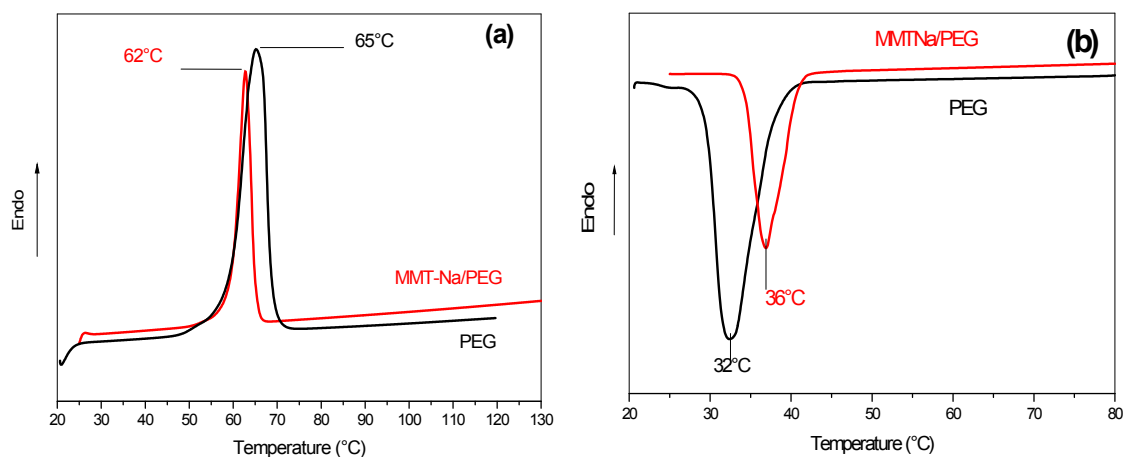

Fig.3. DSC thermograms of PEG and MMT-Na/PEG: (a) heating, (b) cooling.

3.4. Thermogravimetric analysis (TGA)

Fig.4 shows the TGA thermograms of MMT-Na and MMT-Na/PEG. In the MMT-Na thermogram, two major weight loss patterns were observed in the temperature range of 80–130 and 450–750 °C. The first weight loss corresponds to evaporation of adsorbed water.

The second weight loss is due to the loss of structural hydroxyl groups of montmorillonite. The weight loss processes of pure PEG are carried out by only one step from 255°C to 422°C. MMT-Na/PEG nanocomposite shows weight loss in three steps in the temperature region of 80–100, 200–300, and 600–750 °C. A weight loss at 100 and 650 °C is due to loss of water and structural hydroxyl group in the MMT-Na/PEG hybrids, respectively. The decrease of thermal stability of PEG in the nanocomposite is ascribed to the loss in the crystallinity of PEG in the MMT-Na/PEG due to the presence of interactions which hinder crystals growth.
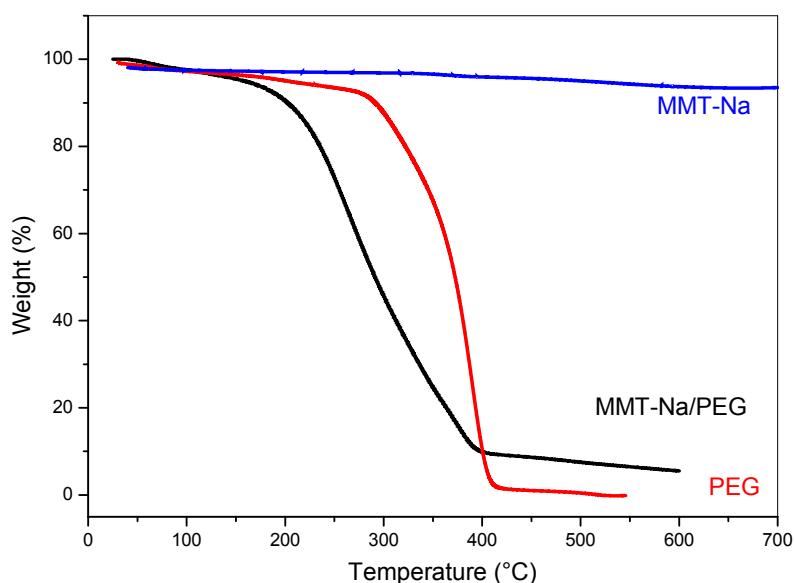

Fig.4. TGA thermograms of PEG, MMT-Na and MMT-Na/PEG nanocomposite.

4. CONCLUSIONS

In this study, PEG has been confirmed to successfully intercalate into the interlayers of montmorillonite. The prepared MMT-Na/PEG nanocomposite was characterized by FTIR, XRD, DSC and TGA analysis.

XRD pattern of MMT-Na/PEG nanocomposite shows an increase in the d-spacing of MMT-Na galleries conforming the good intercalation of the PEG macromolecules.

The DSC study reveals that the clay has acted as a nucleating agent. The clay nanoparticles limit the growth of the PEG crystals suggesting strong interactions between the clay and the macromolecules.

5. REFERENCES

[1] Wang W, Wang A. Nanoscale Clay Minerals for Functional Ecomaterials: Fabrication, Applications, and Future Trends. In: Martínez L, Kharissova O, Kharisov B (eds) Handbook of Ecomaterials. Springer, Cham., 2019.

[2] Brigatti M F, Galán E, Theng B K J, Structure and Mineralogy of Clay Minerals. Handbook of Clay Science,2013, pp. 21–81.

[3] Ghadiri M, Chrzanowski W, Rohanizadeh R. Biomedical applications of cationic clay minerals. RSC Advances, 2015, 5(37), 29467–29481.

[4] Krupskaya V, Sergey Zakusin V, Ekaterina Tyupina A, Olga Dorzhieva V, Anatoliy Zhukhlistov P, Petr Belousov E, Maria Timofeeva N. Experimental Study of Montmorillonite Structure and Transformation of Its Properties under Treatment with Inorganic Acid Solutions. Minerals, 2017, 7(49).

[5] Ray S S, Okamoto M. Polymer/layered silicate nanocomposites: a review from preparation to processing. Prog. Polym. Sci., 2003, (28), 1539-1641.

[6] Ray S S, Bousmina M. Biodegradable polymers and their layered silicate nanocomposites: in greening the 21st century materials world. Prog. Mater. Sci., 2005, (50), 962.

[7] Burmistr M V, Sukhyy K M, Shilov V V, Pissis P, Spanoudaki A, Sukha I V, Tomilo V I, Gomza Y P. Synthesis, structure, thermal and mechanical properties of nanocomposites based on linear polymers and layered silicates modified by polymeric quaternary ammonium salts (ionenes). Polymer, 2005, (46), 12226.

[8] Tanaka T, Montanari G C, Mülhaupt R. Polymer nanocomposites as dielectrics and electrical insulation-perspectives for processing technologies, material characterization and future applications, IEEE Trans. Dielect. Elect. Insul., 2004, (11), 763.

[9] Dabbak S. Z. A, Illias H. A, Ang B C , Abdul Latiff N A, Makmud M Z H. Electrical Properties of Polyethylene/Polypropylene Compounds for High-Voltage Insulation. Energies, 2018.

[10] Kuntmana A, Kuntman H. A study on dielectric properties of a new polyimide film suitable for interlayer dielectric material in microelectronics applications. Microelectronics Journal. 2000, 8 (31), 629-634.

[11] Bhattacharya S.S. and Mandot Aadhar. Studies on Preparation and analysis of Organoclay Nano Particles. Res. J. Eng. Sci. 2014, 3(3), 10-16.

[12] Tiwari R R, Khilar C K, Natarajan U. Synthesis and characterization of novel organo-montmorillonites. Appl. Clay Sci., 2008, (38), 203–208**.**

[13] Silva, I.A., et al., Modification of bentonites with nonionic surfactants for use in organic-based drilling fluids. Appl. Clay Sci. (2014).

[14] Kadajji V G, Betageri G V. Water Soluble Polymers for Pharmaceutical Applications, Polymers. 2011, 3(4), 1972-2009.

[15] Bounabi L. et al., Morphology and thermal properties of clay based biocomposites, J Polym Eng., 2018.

[16] Norrfors K K, Bouby M, Heck S, Finck N, Marsac R, et al., Montmorillonite colloids: I. Characterization and stability of dispersions with different size fractions. Appl. Clay Sci., 2015, (114), 179 - 189.

[16] Bin Ahmad M, Yen Tay M, Shameli K, Hussein M Z, Lim J J. Green Synthesis and Characterization of Silver/Chitosan/Polyethylene Glycol Nanocomposites without any Reducing Agent. Int. J. Mol. Sci., 2011, (12),4872-4884.

[17] Le Forestier L, Muller F, Villieras F, Pelletier M. Textural and hydration properties of a synthetic montmorillonite compared with a natural Na-exchanged clay analogue. Appl. Clay Sci., 2010, (48), 18–25.

[18] Joshi V G, Kevadiya B D, Patel H A, Bajaj H C, Jasra R V., Montmorillonite as a drug delivery system: Intercalation and in vitro release of timolol maleate. International J. Pharm., 2009, (374), 53–57.

[19] Dhanya N, Geena M G, Lakshmi H, Manzoor K., Shantikumar N., Deepthy M., Poly-(ethylene glycol) modified gelatin nanoparticles for sustained delivery of the anti-inflammatory drug Ibuprofen-Sodium: An in vitro and in vivo analysis, Nanomedicine: Nanotechnology, Biology and Medicine, 2013, (9), 818–828.

[20] Ge X G, Wang D Y, Wang C, Qu M H, Wang J S, Zhao C S, Jing X K, Wang Y Z., A novel phosphorus-containing copolyester/montmorillonite nanocomposites with improved flame retardancy, Eur. Polym. J., 2007, (43), 2882–2890.

[21] Zhihong Y, Minghu W, Gang C, Shengjuan L, Panpan P, Qiaolian Z., The Effect of Montmorillonite Modification on Crystallization Behaviour of Polypropylene/Montmorillonite Composites, POLYM POLYM COMPOS, 2016, 5 (24).

[22] Botana A, Mollo M, Eisenberg P, Torres Sanchez P M., Effect of modified montmorillonite on biodegradable PHB nanocomposites, Appl. Clay Sci., 2010, (47), 263–270.

[23] Maiti P, Batt C A, Giannelis E P., New biodegradable polyhydroxybutyrate/layered silicate nanocomposites, Biomacromolecules, 2007, (8), 3393–3400.

How to cite this article:
Baa N., Bouslah Mokhnachi N., Haddadine N., System Based on Clay/Polymer for Biomedical Application. J. Fundam. Appl. Sci., 2020, *12(1S), 108-117.*