Original Research Paper

# Synthesis and Characterizations of MmtO-Copolymer (St-THF) Nanocomposite

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**Abstract:** Nanocomposites are synthesized by one or two polymers and optimized organophilic clay proportions. The aim of Synthesis of the Organophilic clay (montmorillonite) with a two monomers to get a copolytetrahydrofuran- styrene nanocomposite by insitu polymerization. Organophilic montmorillonite (MmtO) was synthesized by ion exchange between $Na^+$ ions in the clay and HDTMAB alkylammonium cations in an aqueous medium. The MmtO were simply dispersed in two monomers: Styrene (St) and Tetrahydrofuran (THF). The Sample was investigated by proton nuclear magnetic resonance (RMN[1]H) and infrared spectroscopy. The nanocomposite exfoliate arrangement of was delved by X-Ray Diffraction (XRD) and Transmission Electron Microscopy (TEM). The temperature degradation was also examined with Thermogravimetric Analyzer (TGA), the thermal stability of nanocomposite higher then polystyrene alone.

**Keywords:** Nanocomposites, XRD, Infrared, RMN and TGA

## Introduction

Copolymer/Mmt nanocomposites denote a novel category of mixed products, which, have been searched expansively for some period and it has been presented that most of the goods are improved in the company of a small quantity of different clay, for example, integration of a limited quantity of Mmt in several search growths the strength and effect barrier goods and thermal degradation, paralleled to pure polymers matrix (Kamal *et al*., 2019; Celik and Onal, 2007; Chavarria *et al*., 2007; Acharya and Srivastava, 2006; Sengupta *et al*., 2007). These advances in the goods are the consequence of dispersion of Mmt in the copolymer and polymer (Tasdelen *et al*., 2008; Jaymand *et al*., 2015). For better dispersion of the Mmt in the matrix, the organic ammonium salt is usually ion-exchanged with the sodium ions in clay for change him to a hydrophobic ammonium. The hydrophobic ammonium surfactant characteristics is principally to increase the interlayer spacing consequently to create area for the matrix to enter into the gallery space during the synthesis of nanocomposites (Anatolii and Gulzhian, 2014; Kong *et al*., 2008; Giannakas *et al*., 2008; Jang and Wilkie, 2005; Niels *et al*., 2019).

While complete compatibility between the long chain of Organophilic montmorillonite (MmtO) and the polymer is obligatory for superior clay dispersion, it have less compatibility with introducing polar groups in the nanocomposite.

The objects of the present study were the preparation of copolymer (St-THF)/Mmt nanocomposite via in situ polymerization.

Firstly, we synthesized and characterized the polytetrahydrofuran, polystyrene and copolymers (THF-St), by optimizing the parameters which permit us to obtain higher yields of copolymers.

Finally, modified Mmt by using a hexadecyltrimethylammonium bromid HDTMAB cationic surfactant. were dispersed in THF and styrene monomers and successively polymerized by in situ polymerization reaction to produce copolymers (THF-St) clay nanocomposite.

## Materials and Methods

### Products Used

The Styrene (St), Tetrahydrofuran (THF) and Acetic anhydride $(CH_3CO)_2O$ traded by Biochem:

- The Acetic anhydride characteristics: d = 1.082; Teb = 140°C; M = 102.09 g/mol

- The tetrahydrofuran characteristics: d = 0.886-0.889, $T_{eb}$ = 65-66.5°C, M = 72.17 g/moL
- The St ($C_8H_8$) characteristics: d = 0.9060, $T_{eb}$ = 145°C, M = 104.14 g/mol

The Maghnite (montmorillonite or Mmt) provided by the company ENOF his CEC:119 meq/100 g.

The HDTMAB salt is traded by Biochem and its chemical formulation is $C_{19}H_{42}Br$, with molar mass M = 364.45. The ebullition point of HDTMAB: $T_f$ = 235°C.

## Sodation and Chemical Activation (Mmt-Na⁺)

10 gr of refined Mmt are distributed in 500 mL of a NaCl media (0.5 N) at high temperature (70°C) for four hours then the mixture of the magnetic shaking is filtered by centrifugation at 3500 tr/min.

The centrifugation is repeated several to realize overload and to get monoionic Mmt. The Mmt-Na⁺ is rinsed many times with distilled water until the declining of the chlorides by $AgNO_3$ confirmed and then it's desiccated, sifted and powdered. In this a process of a cationic exchange that has substituted Na⁺ ions with Ca⁺ and Mg⁺ ions presents initially into the gallery space. The sodium ions had been chosen as compensator ions because they are factor of the inflating and the distribution of the Mmt in water moreover easily hydratable (Niels et al., 2019; Zanetti et al., 2000).

## Intercalation of the Mmt-Na⁺ with HDTMAB (MmtO)

The complete dispersion of MmtO increases the interactions between these two phases and favors the synthesis of nanocomposite.

The alkylammonium salt gives an organophile character with the ions cationic exchange (Na⁺) with the ammoniums cations, we have selected alkylammonium salt as agent of organophilisation HDTMAB is a cationic surface active agent of formula: ($H_3C$–$(CH_2)_{15}$–$N^+$–$(CH_3)_3$, Br).

5 gr of Mmt-Na⁺ is added with three mm mol/g of hexadecyltrimethylammonium bromid, the inorganic-organic mixture is added to 250 mL of distilled water solvent.

The mixture media is positioned in a trial balloon the all in oil-bath at 80°C with the magnetic shaking at 3000 tr/min during four hours, this time is optimized for reactions to be accomplished, then the suspension is filtered and is washed with distilled water for remove the Br ions, then it's desiccated, sifted and powdered.

## Polymerization of Tetrahydrofuran

Ten gr of tetrahydrofuran added to optimized percentage: 1.6 g of $(CH_3CO)_2O$ (15.5% mass of monomer) and 2.5% the Mmt-H⁺, in a flask.

The mixture placed in magnetic shaking preheated to T = 31°C during six hours. The Mmt-H⁺ is recuperate by filtration. The polymer is precipitated in an excess freezing methanol.

## Polymerization of St

In a bottle, 1 g of Mmt-H⁺ dried overnight in an oven, is added to 20 g of treated St. The all was placed in medium with magnetic shaking, the reactional is washed with dichloromethane. The Mmt was filtred by filter paper. The filtrate is then decanted by drop into an excess of methanol consequently the polystyrene precipitate and filtred by filter paper.

## Copolymerization of Poly (THF -St)

In a flask of 100 mL, 0.86 g of Mmt-H+ dried overnight in an oven. added to 10 g of treated St. Mass ratio of tetrahydrofuran added to optimized percentage of. The mixture is placed in an oil bath at 40°C, during six hours under magnetic sharking.

The adding of $(CH_3CO)_2O$ is necessary in the reaction of the polymerization of THF with the styrene (poly (THF-co-St)).

When the reaction time passes, the mixture was diluted in 20 mL of terahydrofuran to eliminate all traces of monomers. then the recuperate is filtered to remove the Mmt (catalyst). The poly (THF-co-St) was precipitated in cooling methanol and dehydrated in the open air and then weighed.

The mass ratios THF/St used are resumed in the Table 1.

## The Preparation of Nanocomposites with Matrix Copolymer

We add in a balloon 3 g of THF and 10 g of Styrene (experiment: mass ratio THF/St = 30/70). 1.6% of $(CH_3CO)_2O$, 5% of MmtO and 2.5% of 4-cyanovlenic acid (-4,4'-Azo-bis)/tetrahydrofuran. The mixture is elevated to 40°C in oil bath under magnetic shaking during 24 h, is considered as sufficient for finishing the reaction of THF-co-St in space layer of MmtO. For eliminate the oligomer and the residual monomer the filtered product is washed with water and methanol.

**Table 1:** The copolymer experimental conditions

| Mass ratio THF/St (g) | 30/70s | | 40/60 | 50/50 |
|---|---|---|---|---|
| Styrene wt (g) | 10.00 | 10.00 | 10.00 | 10.00 |
| THF wt (g) | 2.97 | 2.97 | 4.61 | 6.92 |
| Catalyst wt (g) | 0.65 | 0.74 | 0.74 | 0.86 |
| yield (%) | 40.00 | **42**.00 | 10.00 | 3.00 |

## Results and Interpretation

The powder XRD wiyh the band Kα of Cu, was used in order to confirm the belonging of the Maghnite to the family of montmorillonite and to understand the changes that took place after having Intercalation of $Na^+$ ions.

Figure 1 indicates the X-ray diffraction arrangements of the Mmt (1) and the MmtO (2). A development of the basal spacing $(d_{001})$ of MmtO after the insertion of the HDTMAB. Exactly, the pure Mmt shows a $d_{001}$ spacing of 12.6Å. In the case of the Mmt-O, the $d_{001}$ advance to 18.53Å.

The Fig. 2 characterize IR spectra of the MmtO. In the spectra of Mmt-O, the presence of all characteristics picks of pure Mmt with also the presence of characteristics of HDTMAB surface active by the appearance of a band of less force at 1472.91 cm$^{-1}$ relate to linking $CH_3$-N and the two bands of average intensity absorption located at 2918.15 and 2849.55 cm$^{-1}$ respectively to stain attributed of grouping $-CH_2$ et $-CH_3$.

### Characterization of PTHF

### IR Spectroscopy

The IR spectrum of the polyTHF represented in Fig. 3, the absorption bands detected in the spectrum of polyTHF (Belbachir and Bensaoula, 2001; Ouis *et al.*, 2004). The absorption bands observed in the spectrum of PTHF, have already been identified in the literature and correspond to the carbonyl group (C = O) of ester at 1741 cm$^{-1}$, at the vibrations of the C-H joining of methyl group at 2858 cm$^{-1}$, the existence of the ether function C-O, is confirmed by the band situated at 1113 cm$^{-1}$.

The study of the system THF- anhydride acetic – Mmt-H$^+$ illustrate that the quantity of Maghnite H$^+$

affects the yield and the molar ratio THF/acetic anhydride = 8.84 gives a yield of 50% of Polytetrahydrofuran.

### Characterization of PSt

### RMN$^1$H

Polystyrene was described by RMN$^1$H (200 MHz). The different protons ($^1$H) observed and their chemical displacements are cited in Table 2.

We also observe in spectrum of RMN$^1$H a singlet situated about 1.2 ppm which relates to $CH_3$- of chain end (Fig. 4).



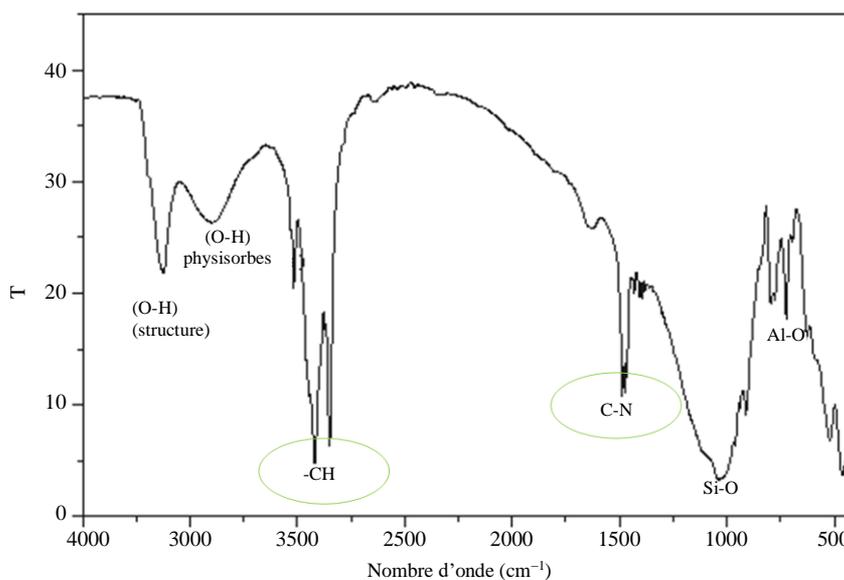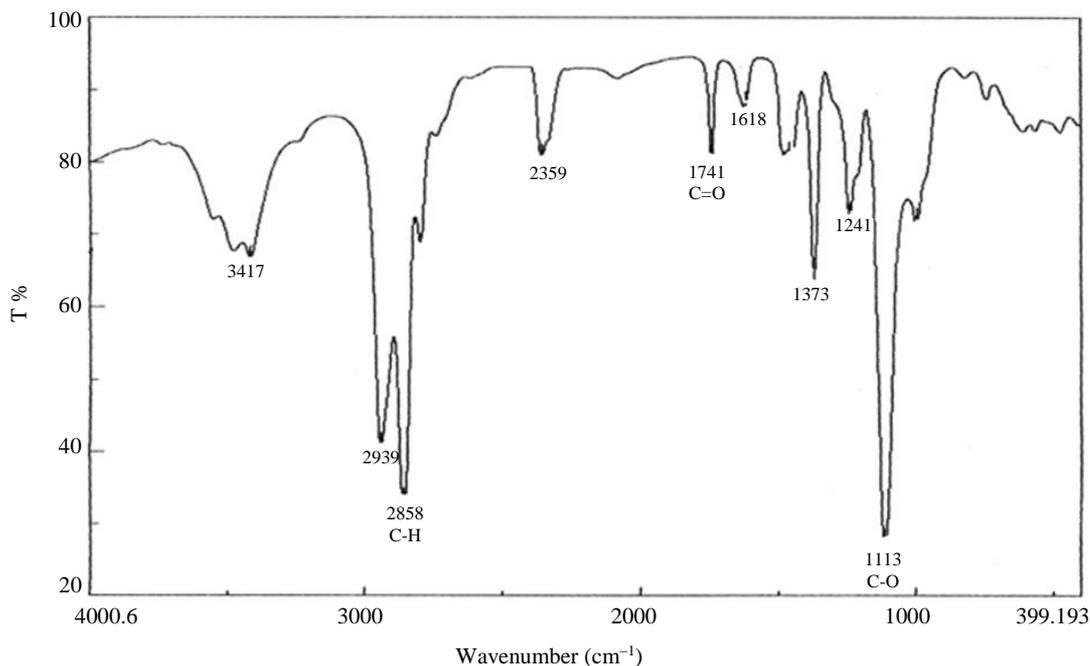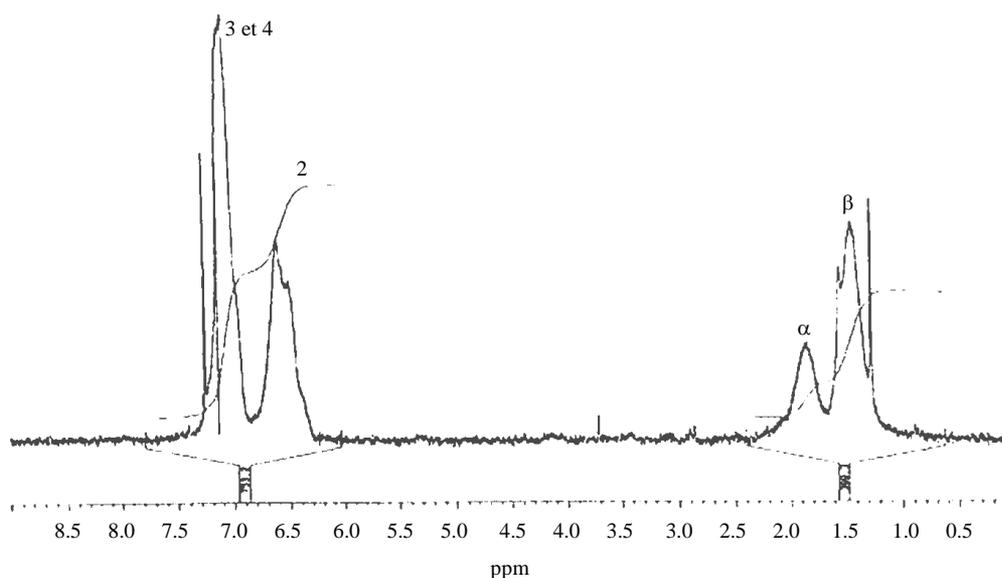**Fig. 1:** XRD patterns of the parent Mmt (1) and the MmtO (2)



**Fig. 2:** IR spectrum of the organophilized montmorillonite (Mmt) by the HDTMB

**Fig. 3:** IR spectrum of PTHF



**Fig. 4:** RMN 1 H band of polystyrene

The second protons of the end chain are overlapped with the $^1$H of polySt chain.

Additionally, the RMN$^1$H spectrum, have allowed us to evaluate the molar mass of polySt by comparing the integration of aromatic $^1$H of the nucleus $I_a$ situated between 6.3 and 7.25 ppm to those of CH3- protons $I_m$ of chain end.

We then discovery an average weight of about 2100 and $I_a/I_m = 17$.

*IR Spectroscopy*

The Fig. 5 approves the nature of the polymer by identifying IR characteristic bands of PolySt before cited in the literature.

The benzene nucleus signs its elongation existence at 3100 cm$^{-1}$ and at 695-755 cm$^{-1}$ appear clearly the deformation. The band positioned at 2921 cm$^{-1}$ is attributed to the stretching of the C-H linking in the

groups of the $C_2H_4$ and $= CH_2$. The band situated at 1480 $cm^{-1}$ characterizes the $-CH_3$ group of chain end. Finally it's absence of the double joining of monomer Carbone (1680 $cm^{-1}$).

### Thermogram DTA-GTA

Thermogram TG of the pure PS shows a loss of mass of 15% between 59°C and 116°C allotted to hygrometrical water and the beginning of no residual solvent in the finished product which is methanol. It is also noted that the polystyrene decomposition starts starting from 340°C (Fig. 6).

### Characterization of the copolytetrahydrofuran-Styrene

### Infrared Spectroscopy

The Fig. 7 presented IR copolymer analysis with 30/70 weight ratio, spectra illustrate the key functions such as the ester existence in the acetate in 2 parts: at 1735.79 $cm^{-1}$ in the function $C = O$ and at 1185.89 $cm^{-1}$ to group the C-O.

On 3 bands Styrene phenyl, double linking of Carbone at 1597 $cm^{-1}$, another at 3028.3 $cm^{-1}$ for connection C-H and the last the deformation in the plan of C-H at 755 $cm^{-1}$.

The ether function appears clearly at 1070.79 $cm^{-1}$.

The large band at 3720.3 $cm^{-1}$ is attributed to the linking O-H, probably due to a few dehydrating of K-Br utility.

### RMN[1]H

The copolymer obtained (mass ratio of THF/St = 30/70 with 2.5% Mmt-H^{+} and 15-17% af A.A. related to a mass of tetrahydrofuran was characterized by RMN[1]H at 300 MHz.

A chemical displacements of diverse ^{1}H existent in the sample allowing to the RMN[1]H in $CDCl_3$ solution are given in Table 3 and Fig. 8.

The interpretation summarized in Table 3 approves that the obtained sample is copolytetrahydrofuran styrene by the existence of 2 motifs St and tetrahydrofuran.

Figure 8 represents also the reactional mechanism proposed copolymer obtained thus that the position of the grafting of styrene on the THF. It is noticed that the Acetic Anhydride (AA) is at the end of chain.

### Characterization of MmtO Copolymer Terahydrofuran Styrene Nanocomposite

The infrared spectra of the pure polySt (1) and/Mmt-org nanocomposite copolymer tetrahydrofuran styrene (2) are presented in the Fig. 9. The IR spectra of nanocomposite and bands of polySt show the specific absorption groups at 3,100-2,850 $cm^{-1}$ for stretching vibration of connection -CH, fragile aromatic implication and groups ensembles in the 2,100-1,650 $cm^{-1}$ section, stretching vibrations of double connection Carbone at 1,606 $cm^{-1}$ and 1,510 $cm^{-1}$. Apparently the infrared spectra of nanocomposite demonstrate the amalgamation of Mmt-org and two polymer. The bands characteristics with the structure of the polyTHF relate to carbonyl grouping C $= O$ of ester of 1775 $cm^{-1}$, the existence of ether linking C-O is definite by the located group of 1240 $cm^{-1}$. Mmt appears by a band of Si-O stretching to 1080 $cm^{-1}$.

The bands about 1,636 $cm^{-1}$ and 3,600 $cm^{-1}$ are due to the O-H groups in the montmorillonite. The IR spectrum approves that the organophile Mmt-org have been fixed into matrix during the polymerization and consequently forms the nanocomposite.

**Table 2:** Chemical displacements of different protons in the polystyrene ($CDCl_3$)

| δ (ppm) | Attribution |
|---|---|
| 6.9-7.25 | $1H_4+2H_3$ |
| 6.3-6.8 | $2H_2$ |
| 1.86 | $H_\alpha$ |
| 1.3-1.65 | $2H_\beta$ |

**Table 3:** Chemical displacements of RMN[1]H copolymer protons in $CDCl_3$ solution and 300 MHz frequency

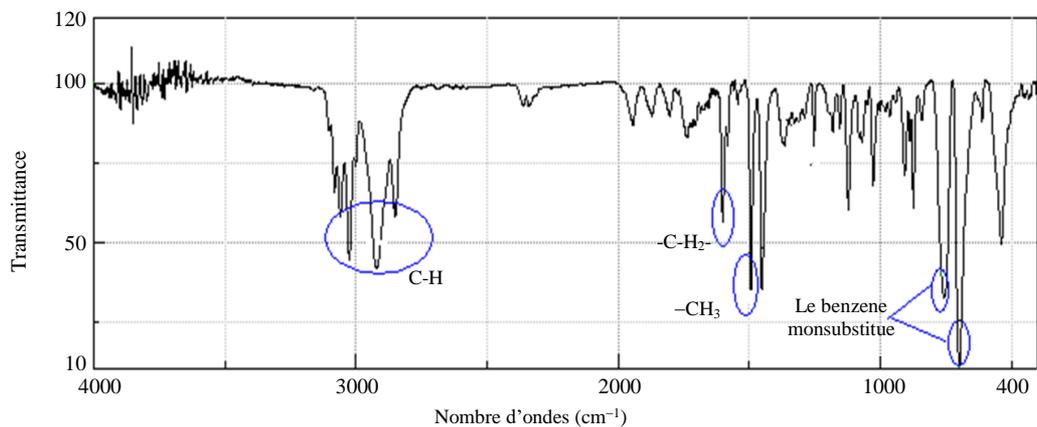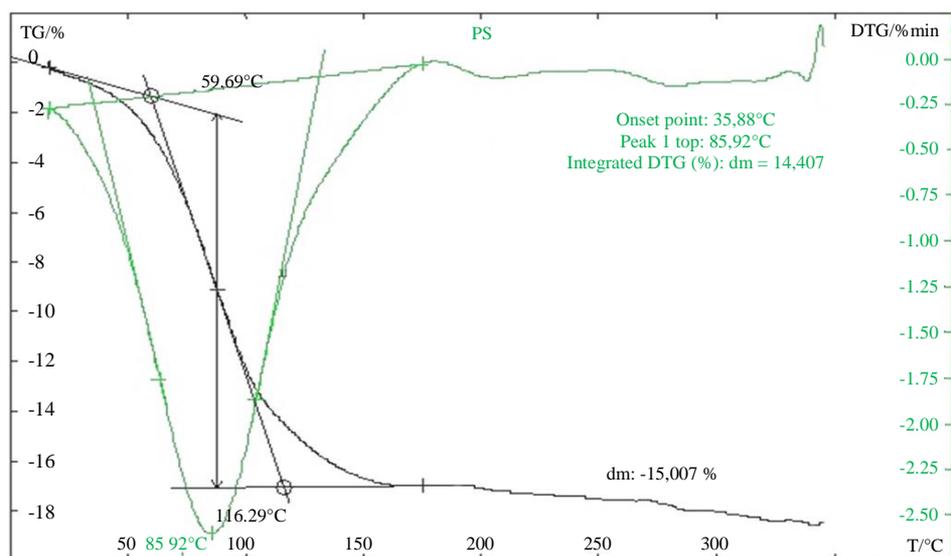| Indication | Pattern | Nature of the proton | δ ppm | |
|---|---|---|---|---|
| | | | Theory | Experiment |
| a | St | Ph-**CH-** | **1,6-2,7** | 1,875 |
| b | | Ph-CH-**CH2** | **1,2-1,8** | 1,461 |
| c | | 2H (en ortho du phényle) | 6,0-8,0 | 6,611 |
| d,e | | 3H (en méta et en para du phényle) | 6,0-8,0 | 7,075 |
| f,i | THF | -O-**CH2**CH2CH2**CH2**-O- | 3,3-4,0 | 3,448 |
| g,h | | -O-CH2**CH2CH2**CH2-O- | 1,2-1,8 | 1,645 |
| j | | **-CH2**O-CO-CH3 | **3,9-4,6** | 4,116 |
| k | AA | -CH2O-CO-**CH3** | 1,8-2,6 | 2,079 |

**Fig. 5:** IR spectrum of polystyrene
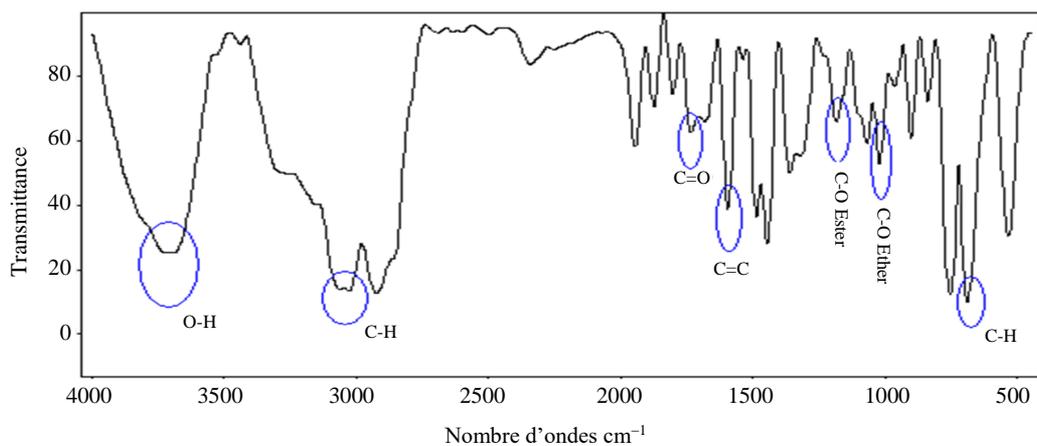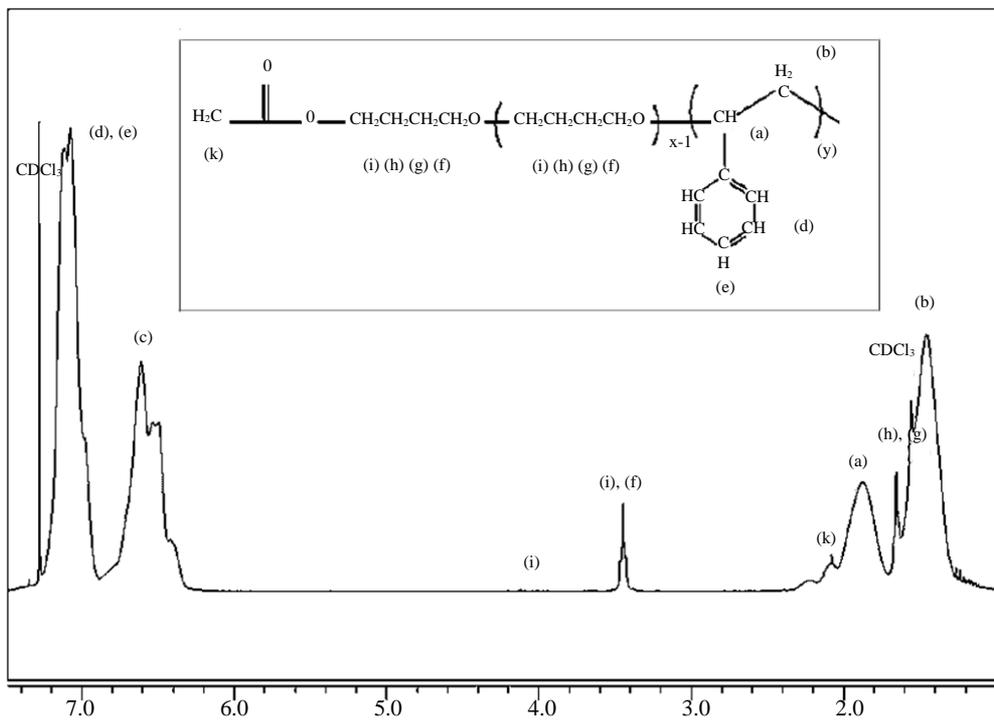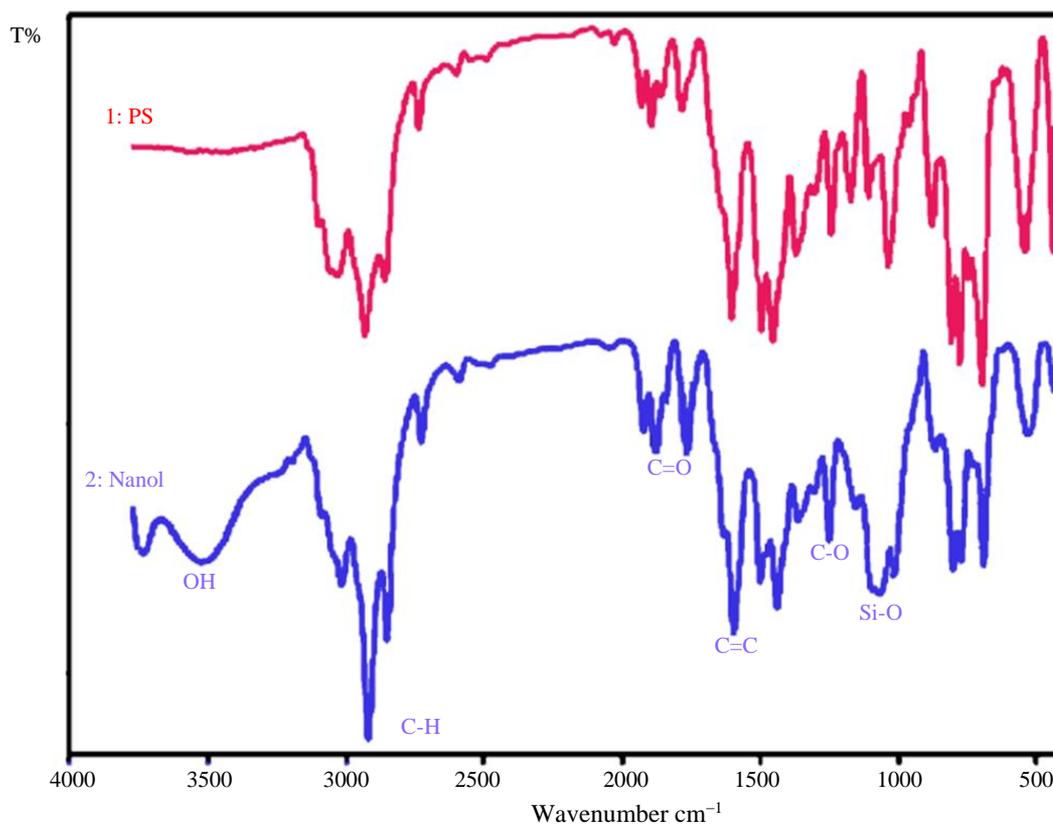


**Fig. 6:** Thermogram of polystyrene



**Fig. 7:** Infrared spectra of copolymer THF-St

303

**Fig. 8:** RMN1H spectrum (300 MHz) of poly (THF-co-St), solvent $CDCl_3$



**Fig. 9:** Infrared spectrum of the polySt (1) and copolymer (St-THF)/Mmt nanocomposite (2)

X-ray diffraction, XRD, shown data on the differences of $d_{001}$ of Mmt. The realization of an intercalated arrangement must effect in a reduction of 2theta, indicating a growth in the inter layer spacing, the realization of an exfoliated assembly in the whole loss of no peak of XR Diffraction. In more or less cases, a disordered arrangement is gotten and this also demonstrate no band, thus the nonappearance of a band cannot be confirmed the exfoliated of sample. So, frequently transmission electron microscopy TEM is obligatory. The XR Diffraction arrangements for the Mmt-org nanocomposite (THF-St) offered in Fig. 10, the absence nanocomposite of peaks. In conclusion the sample could be either that an exfoliated or an immiscible nanocopolymer

*TEM Microscopy of Nanocopolymer*

TEM microscopy shows the morphology appearance of the nanocopolymer (Fig. 11). XRD and TEM is complementary method, principally in the absence of diffraction peaks of $d_{001}$. The TEM digit of nanocopolymer exhibit the clair sections characterize copolymer and the black appearances specify Mmt. It is essential to aspect at the relations Mmt and matrix, Mmt and HDTMAB and between copolymer and HDTMAB. A finest equilibrium of altogether interfaces normally proves to an exfoliated nanocopolymer. A TEM microscopy micron sized Mmt Tactoids are absent because of growth and enlargement by matrix and nanocomposite sample.

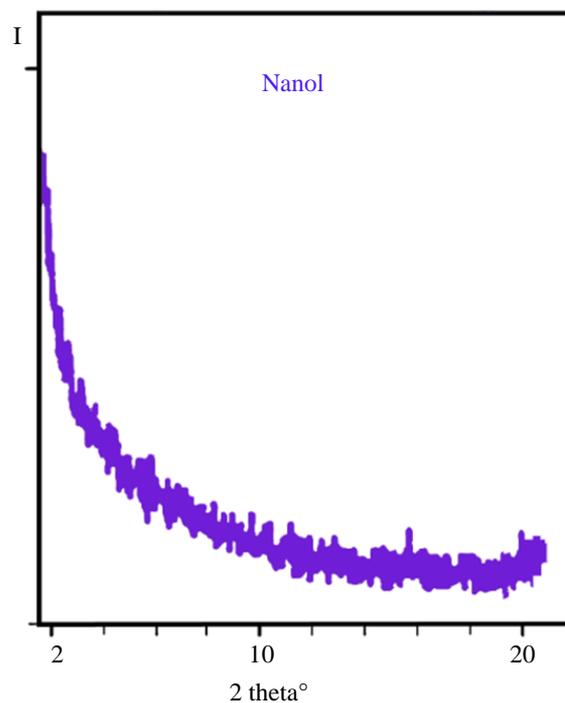This defined an exfoliated morphology for the nanocomposite.



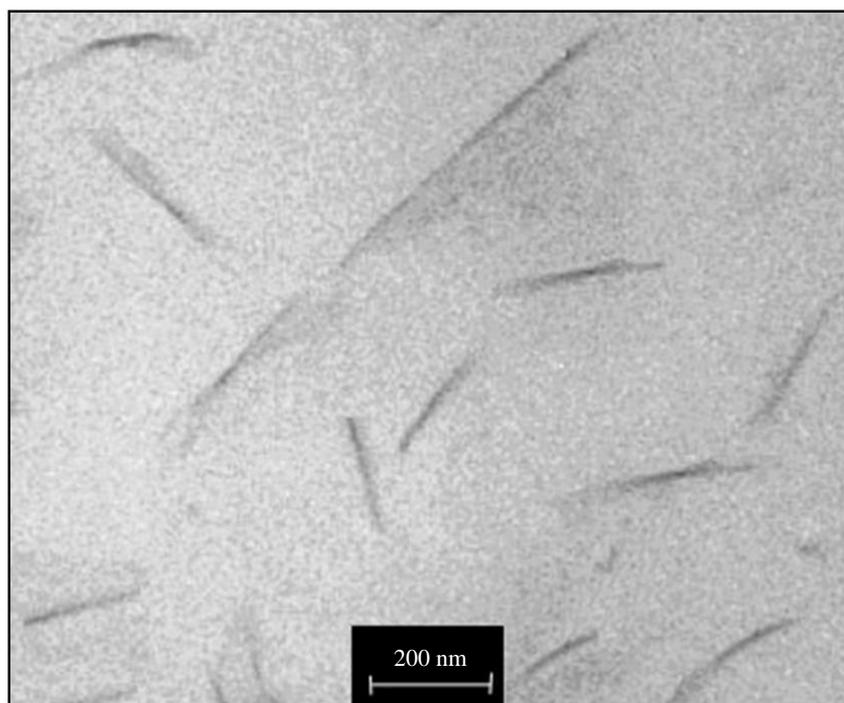**Fig. 10:** XR Diffraction of the (THF-co-St)/MMT nanocomposite



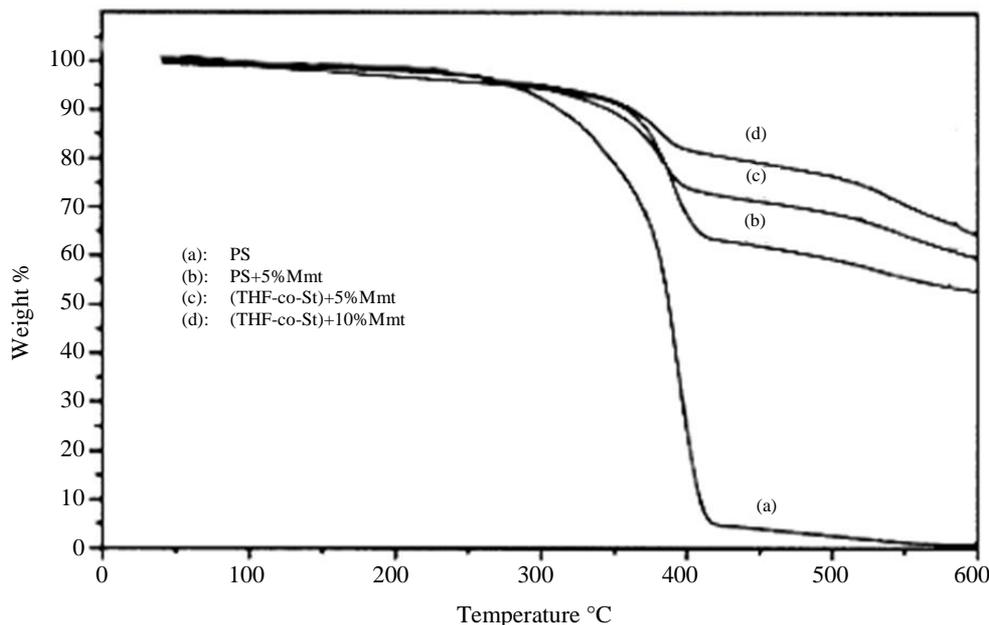**Fig. 11:** TEM microscopy of Mmt-org nanocomposite (THF-St)

**Fig. 12:** TGA thermograms of nanocomposite and Pure PS

*Thermal Propriety of Nanocopolymer*

TGA bends of PS and (THF-St)/MMT nanocomposite are revealed in Fig. 12 (a-d). TGA effects show progress of the thermal propriety for (THF-co-St)/MMT nanocopolymer with a polySt. The records of the beginning of the thermal degradation is 5%, the medium of this degradation for polystyrene is 50% and the rest that was at 600°C, were moved to upper in nanocoplymer. The rest that was at 600°C, for polystyrene + Mmt (5%), (THF-co-St)/MMT (5%) nanocomposite and (THF-co-St)/MMT (10%) nanocomposite were 55 wt%, 60 wt% and 65 wt% respectively. Thus the weight persisted at 600°C, representing that the Si generate the barrier effect which delay the degradation of the nanocomposites.

This effect is amplified with the increase of the addition of MMT according to deferent applications.
The thermal behavior of nanocopolymer is made by the degradation of the HDTMAB. In the thermal behavior of sample at higher heats, acidic $^1H$ sites are made via the Hoffman decomposition of the HDTMAB of Mmt, giving protonated Mmt (Mohammad *et al.*, 2017; Qi *et al.*, 2005; Camino *et al.*, 2005; Arat and Uyanık, 2017).

# Conclusion

The most important result from this work is the formation of the copolymer (St-THF) and the exfoliated (THF-St)/organo-modified montmorillonite nanocomposite was well prepared by in situ polymerization and diffusing Mmt that was modified with a HDTMAB in St and tetrahydrofuran monomers.

For the formation of the copolymer we have to propose a structure approximate according to NMR analyses, the diverse factors studied had little effect on the attaching in the copolymers, it is possible, so, that the increasing chains are found in a compound system.

The TEM and X-ray diffraction investigates exhibited that the (THF-St)/Mmt nanocopolymer has a completely exfoliated arrangement and the Mmt-org layers were well distributed in the copolymer. The thermal behavior of (THF-St)/Mmt nanocopolymer enhanced visibly in comparison with polySt and PTHF. In deduction, the exclusive goods of the nanocoplymer product from the solid contacts between the Mmt-org structural layers and the chains of matrix.

# Author's Contributions

**Hattab Youcef:** Make considerable contributions to conception and design and acquisition of data and Analysis and interpretation of data and give final approval of the version to be submitted and any revised version.

**Hakiki Ouahiba:** Coordinated the data-analysis and contributed to the writing of the manuscript.

# Ethics

This article is original and contains unpublished material. The corresponding author confirms that all of the other authors have read and approved the manuscript.

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