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REVIEW

Thermal stability and structural characteristics of PTHF–Mmt organophile nanocomposite

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KEYWORDS

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IR;
Organophilisation

Abstract Polymer nanocomposites represent a new class of material alternative to conventionally filled polymers. This new class of material is synthesized from a mixed polymeric matrix at a weak percentage with montmorillonites as inorganic charges. Their dispersion is facilitated by the organophilization of their structure by the exchange of inside foliar cations with compatilization possessed at once hydrophiles and hydrophobes ends, respectively, to be compatible with clay and polymer.

The objective of this study is to use organophilized montmorillonites in the presence of monomer tetrahydrofuran to obtain polytétrahydrofuran montmorillonites (PTHF–Mmt) of composites by polymerization in situ. The organophilisation of the Mmt is formed by active cationic surface. The obtained results show an increase in the distance inside the reticular in the diffractograms of X-rays (DRX) and the appearance of absorption bands of the characteristics of polytétrahydrofuran on the spectra of infrared spectroscopy (IR), which indicate pre-polymerization of tetrahydrofuran in the galleries of clay and, therefore, the obtaining of a nanocomposite. We have also studied the thermal stability of the samples by differential analysis calorimetric (DSC) analysis, and we can conclude that the nanocomposites are stabilized thermally by the presence of clay in the matrix.

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Contents

1. Introduction

The uses of clay mineral are many and varied, in civil engineering, they are used so far as industrial materials (refractory, construction materials) in agronomy as fertilizers thanks to their properties of hydration and adsorption, in chemistry, they are often used as a catalytic support. Whatever the discipline, recrystalline structure of clay is important because, it is responsible for the specific properties of mineral. The term nanocomposite is a recent creation, but the concept is not new (Costa, 2001; Hartmut, 2003; Abou El-Nour et al., 2010) the composites with the micrometrics renforts have shown some of their limits, their properties which resulted from the composite:

The improvement of the resistance for example is detrimental to the plasticity or the optic transparency.

The nanocomposites could palliate some of this limit and present the advantages of the classical composite to the micrometrics renforts:

- A significant improvement of mechanic properties (Kojima et al., 1993).
- Thermal conductivity growth and varied properties especially optics that is not explained in the classical approaches of the components (Alexandre and Dubois, 2000).

The nanoparticles have inferior dimensions of wave length of the visible light (380–780 cm^{-1}) that allow materials to preserve the departure of their optical properties as well as the pre good state of the surface (Vaia and Giannelis, 2001; Tasdelen et al., 2010).

The diminution of the size of the renforts that we insert in the matrix lead to the important growth of the surface of the interfaces in the composite, or exactly this interface which controls the interaction between the matrix and the renforts, explaining a part of the odd nanocomposites properties.

The odd nanometric particle in a notable manner improve, but some properties with voluminal fraction are weaker than the micrometric particles.

It is in this context that we enrolled this study about the synthetic and the characterizing of clay polymer nanocomposite.

The objective of this work is to better understand the role of the interface between loads and matrix.

We have chosen to elaborate the nanocomposites materials by polymerization in situ, using such matrix a usual thermoplastic polymer, the polytétrahydrofuran.

The load chosen is the montmorillonite modified. The montmorillonite is the ideal load for the valorisation at lower price of the polymer materials.

2. Experimenting

2.1. Used productions

Acetic anhydride $(CH_3CO)_2O$ and the tétrahydrofuran, commercialized by BIOCHEM the montmorillonite (Mmt) with a CEC of 119 meq/100 g.

The bromide of hexadecyltrimethylammonium (HDTMAB) is commercialized by Biochem and its chemical composition is $C_{19}H_{42}BrN$, Its molar mass M = 364.45 and its point of ebullition $T_f = 235\,°C$.

2.2. Chemical activation: sodation (montmorillonite Na^+)

Ten gram of purified montmorillonites are dispersed in 500 ml of a solution of NaCl (0.5 N), at 70 °C for 4 h and the product of a reaction is filtered by centrifugation at 3500 tr/min.

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The operation is repeated thrice to attain saturation and to obtain monoionic clay. The montmorillonite is washed several times with distilled water until the disappearing of the chlorides tested by $AgNO_3$, and then it's dried, pounded and sifted. It is by a process of a cationic exchange that has replaced the sodium ions with calcium ions and magnesium presents initially in the galleries of interfoliaires. The sodium ions had been chosen as compensator ions because they are more easily hydratable and favour the inflating and the dispersion of the montmorillonite in water (Zanetti et al., 2000; Schmidt et al., 2002).

2.3. Intercalation of the sodic montmorillonite with an organic molecule

The elaboration of nanocomposite is conditioned by a complete dispersion of the silicates plaquette in the polymer matrix in order to increase the interactions between these two phases. The sodic clay is processed by alkylammonium salt which gives an organophile character with the ions cationic exchange (Na^+) with the ammoniums cations. For these syntheses we have chosen as agent of organophilization; the bromide of hexadecyltrimethylammonium (HDTMAB) a cationic surface active agent of formula: $(H_3C–(CH_2)_{15}–N^+–(CH_3)_3,Br^-)$.

Five grams of sodic montmorillonite is mixed with 3 mm mol/g of HDTMAB, the inorganic/organic mixing is addedto 250 ml of distilled water that is used like a solvent, the montmorillonite here present, therefore, excellent inflating properties in suspension, better aptitudes for a cationic exchange. The mixing is placed in a trial balloon plunged in oil bath that raises at 80 °C.

The magnetic shaking (3000 tr/min) is kept during 4 h; this time is optimized for reactions to be completed. After the cationic exchange, the suspension is filtered the recuperated organophilized montmorillonite is rinsed with distilled water to eliminate the bromide ions, it is then dried, pounded and sifted.

Table 1 The nanocomposites elaboration of experimental conditions.

$m_{[THF]} = 10$ g, % $(CH_3CO)_2O = 4\%$, time of reaction = 24 h, $T = 40$ °C $\Delta m = 0.01$ g, $\Delta T = 1$ °C	
$MmtH^+$ = Mmt acidified with HCl (0.2 N)	
Samples	Used acid
NANOT1	H_2SO_4 (1 N)
NANOT2	–
NANOT3	HCl (1 N)
NANOT4	$HClO_4$ (1 N)
NANOT5	$AlCl_3$ (1 N)
NANOT60	HOOCCH=CHCOOH (1 N)

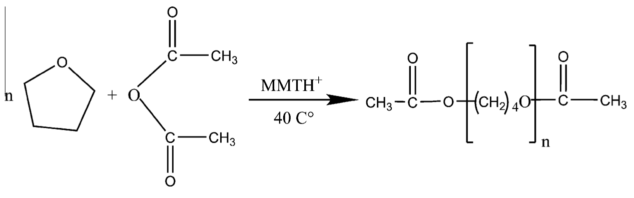

Figure 1 The reactive diagram of polymerization of THF with the presence of $MmtH^+$.

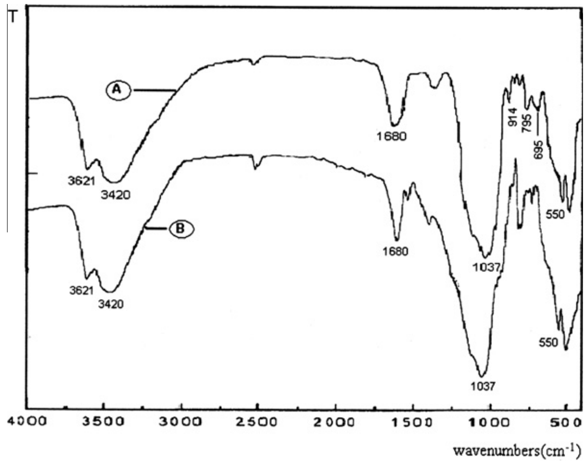

Figure 2 IR spectra of montmorillonites: Natural and sodic.

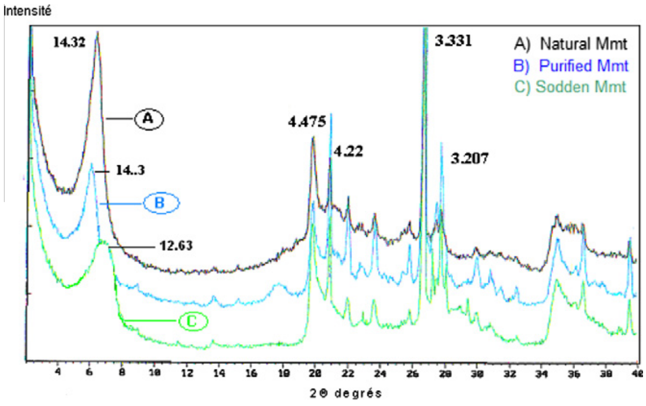

Figure 3 RX diffraction of clay.

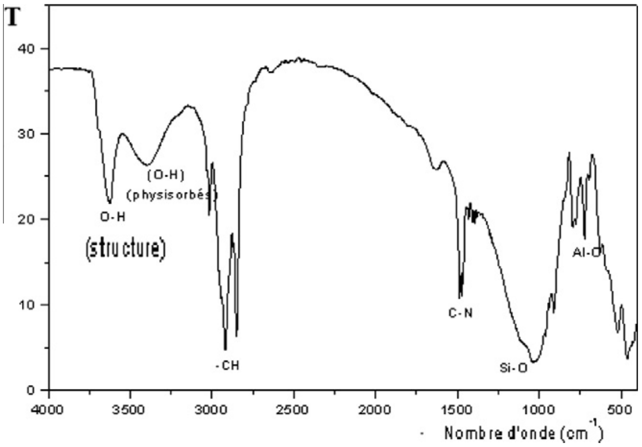

Figure 4 IR spectrum of the organophilized montmorillonite by the HDTMB.

2.4. Polymerization of THF

We add to 10 g (0.138 mol) THF and 0.4 g (0.0039 mol) of acetic anhydride (4% from mass of monomer) the organophilized Mmt, in variable amounts in a balloon. The preliminary reactions have allowed to optimize the quantity of acetic anhydride in the reactive mixing.

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The rate chosen for the following of our work is fixed at 4% with mass, the value that permit a rate of optimal conversion.

The amounts of Mmt vary from 1% to 15% in relation with the mass of monomer. The reactions are effected under magnetic shaking, at $T = 40 \pm 2$ °C, for the time of variable reactions, the Mmt is recuperated by filtration. The polymer is precipitated, in an excess of methanol at cold then dried in free air. We have started with synthesizing of polytétrahydrofuran (PTHF) from tétrahydrofurane (THF) by using the montmorillonite as catalyst, in this case, the reaction of polymerization have no places (Fig. 1).

In addition to the acetic anhydride being indispensable, it is allowed to carry out the polymerization of THF in the presence of the montmorillonite processed according to the reactive mechanism represented below (Belbachir et al., 2001; Ouis et al., 2004; Tasdelen et al., 2008).

2.5. The preparation of nanocomposites with matrix PolyTHF

2.5.1. Mode of operation

We add in a balloon of 10 g (0.138 mol) of THF and 0.4 g (0.0039 mol) of acetic anhydride, 5% of organophile montmorillonite and 5% of acid (several acid is used). The mixing is raised to 40 °C in an oil bath. The reaction is held under magnetic shaking during 24 h. This lasting time is considered as enough for completing the interaction of PTHF in interlayer space of organophile clay. The suspension is filtered; the product obtained is washed with water and methanol in order to eliminate the oligomer and the residual monomer. The experimental conditions used are resumed in the Table 1.

2.6. Measures

As it shows the spectrum of the sodic montmorillonite carried back in Fig. 2. The same indicated the absorption as that of natural clay, however we note that the absorption bands, spread out from 600 to 900 cm^{-1} increase in intensity which is due to the disappearance of impurity.

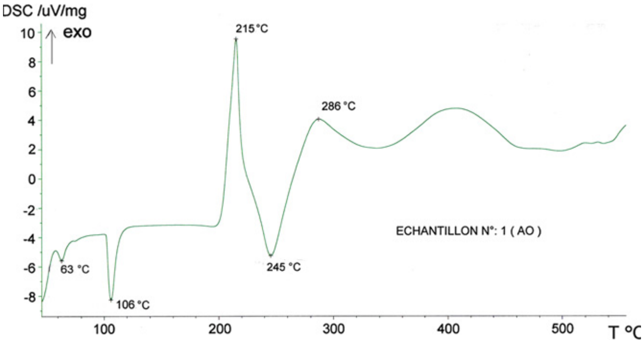

Figure 5 The DSC thermogram of organophilized clay (Mmt–HDTMAB).

Table 2 The moving in DRX of the spoke d_{001} for used clay.

Clay	Cations and intercalated molecules	The position of the d_{001} in Å
Natural	Mg^{++}, H_2O	14
Sodden	Na^+	12
Intercalated	HDTMAB	20

The (DRX) are realized with the help of diffractometer of Philips type pw, 1700, worked with the monochromatic K_α of copper (1.5406 Å).

The parameters chosen have a weak speed of rotation with a step of 0.05°, the observed domain of the angle 2θ° is understood between 2° and 40° for the brute montmorillonites, purified, sodden and organophilized (Fig. 3).

3. Results and discussions

3.1. Characterization of the organophile montmorillonite

We take up on Fig. 4 the appearance of all characteristics bands of Sodden montmorillonite with also the appearance of characteristics of surface active by the manifestation of a pick of less intensity at 1472.91 cm^{-1} correspond to joining CH_3–N and the two bands of average intensity absorption situated at 2918.15 and 2849.55 cm^{-1}, respectively, to stain attributed of grouping –CH_2 et –CH_3.

We observe in the diffractogram of the organophilized RX (Fig. 9) a clear moving of pick of diffraction towards the small angles from 7° to 4.4°), which translate a raise of distance between leaves of 12.63 Å for sodden clay at 19.79 Å in those are intercalated by the HDTMAB.

The separation is due to the substitution of sodium by the molecule of HDTMAB utilized for cutting more important which engender this expansion of interfoliaire galleries. The Table 2 gives the moving of the d_{001} for used clay.

Lagaly and other researchers (Lagaly, 1986; Komori and Kuroda, 2000) describe the probable confirmations of alkylammonium ions to the surface of leaves, according to the length of the carbonaceous chain and the deficit charges of a leaf, they could organize in monostratum and in bistratum follow a pseudotrimoleculaire arrangement or a paraffinic type. We speak about monostratum when adsorbed ions on a leaf surface cover less than half of the surface of this one. In this case, the substituted ions of two adjacent leaves are situated in the same plan. This structure is characterized by an interfoliaire distance about 14 Angstroms when the surface cover of

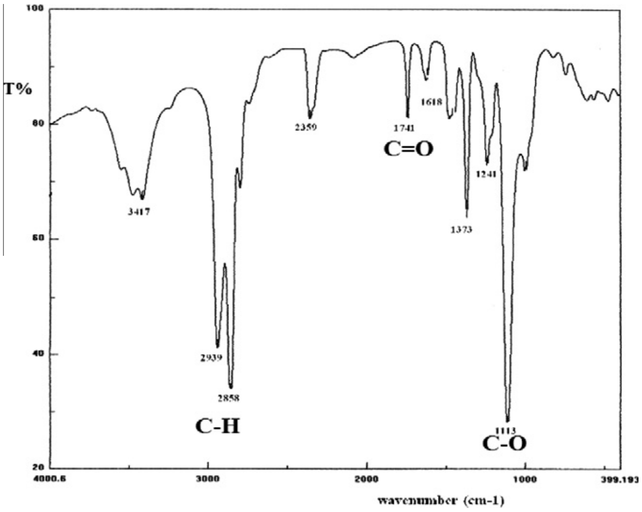

Figure 6 IR spectrum of PTHF obtained after 24 h of reaction.

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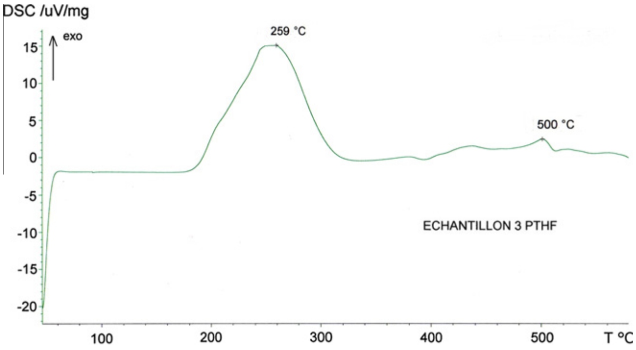

Figure 7 DSC thermogram of PTHF.

the ions is upper in half of the surface of leaf, The alkylammonium ions of two leaves facing each other organize in bistratum. The interfoliere distance is nearly 18 Å. If the substituted alkylammonium ions possess a long carbonaceous chains for steric congestion causes, these chains organize in a pseudotrimoleculaire arrangement. The interfoliair distance in this case is about 22 Angstroms. Finally we talk about an arrangement of parafinic type when the quantity of adsorbed ions is important and the steric congestion (bound in length of the chain and in the presence of grouping or of interacted molecules with the leaf surface), draw a re-erecting of carbonaceous chains. The distance between leaves varied then according to the length of carbonaceous chain and the inclination of angle of chains with regard to the surface of leaf.

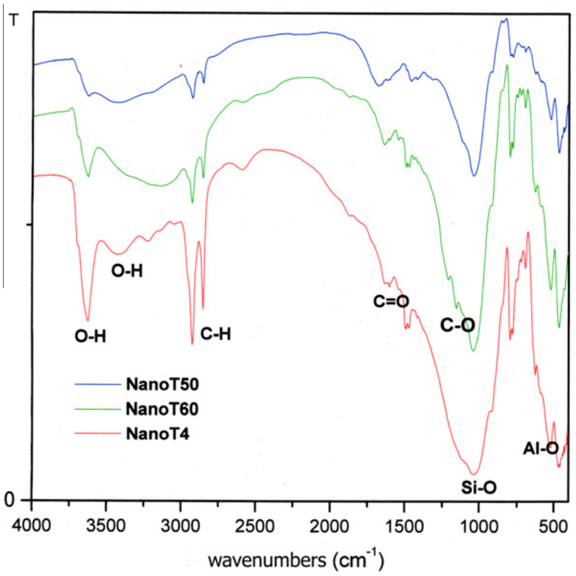

Figure 8 Infra-red spectra of organophile nanocomposites PTHF–Mmt.

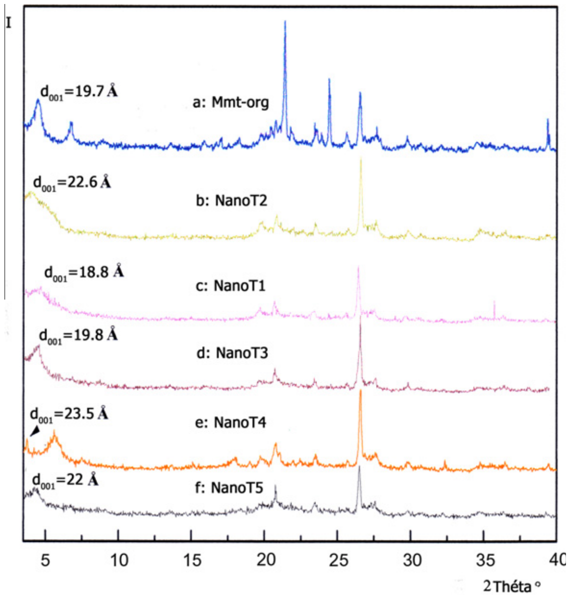

Figure 9 RX diffractograms of organophile nanocomposites PTHF–Mmt.

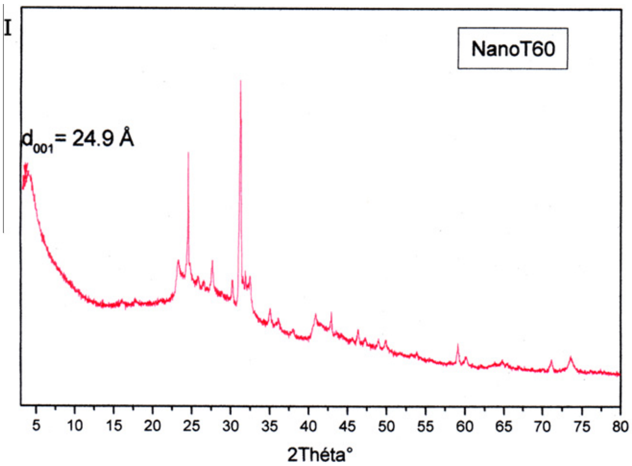

Figure 10 RX diffractogram of synthesized organophile nanocomposite PTHF–Mmt with $C_4H_4O_4$ (1 N).

According to the results of DRX the $d_{001} = 21$ Å. The most probable conformation of chains is the pseudotrimoleculaire organization. The thermic behaviours of the organophile montmorillonite are analysed by deferential calorimetric analysis (DSC). This technique of analysis (DSC) permits to record all the changes of states or the transition of the sample when it is submissive to a cycle of temperature. We have used a type of appliance (DSC) 200 PC NET ZSCH. The measures have realized between 50 and 580 °C, with a speed of 20 °C/min.

The first endothermic phenomenon centred in 106 °C is associated with a departure from physisorbed water. Towards 245 °C, we observe a great deal of an endothermic pick due to the fusion of active surface; this pick is preceded by an effect of exothermic of active surface. Less than 286 °C of an exothermic intense effect which is shown in Fig. 5 would be attributed to the graduation of modifying ions of active surface.

3.2. Characterization of PolyTHF

3.2.1. IR spectroscopy

Fig. 6 represents an IR spectrum of an obtained polymer. The bands of observed absorption in the spectrum of PTHF, that are identified in the literature (Ranjan and Brittain, 2007)

Table 3 resume of results of DRX and obtained of nanocomposites nature.

Nanocomposites	d_{001} (Å)	Morphology
NANOT1	18.8	–
NANOT2	22.6	Intercalated
NANOT3	19.8	Intercalated
NANOT4	23.5	Intercalated
NANOT5	22.0	Intercalated
NANOT60	24.9	Intercalated & exfoliated

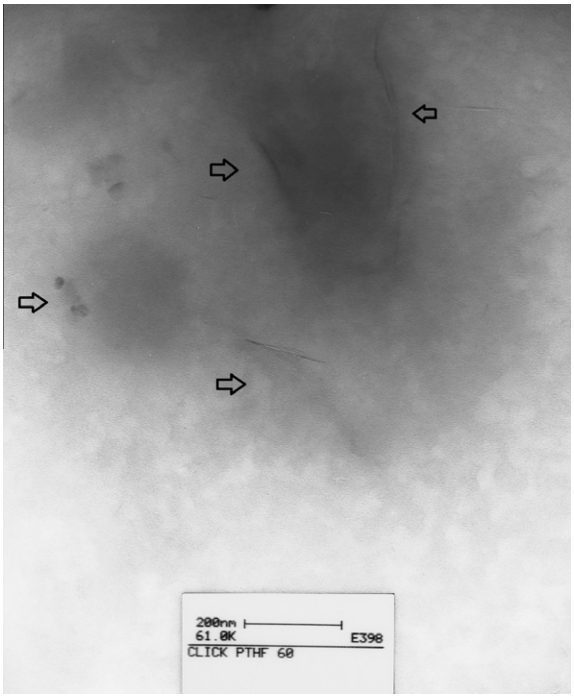

Figure 11 TEM image of organophile nanocomposite PTHF–Mmt with $C_4H_4O_4$ (1 N).

and correspond to carbonyl grouping (C=O) of ester of 1741 cm$^{-1,}$ at joining vibration C–H of methyl grouping of 2858 cm^{-1} the presence of ether function C–O is confirmed by the situated band of 1113 cm^{-1}.

3.2.2. Differential calorimetric analysis (DSC)

The study of the degradation of polymers allows to very often to step in the factors tended to ameliorate their thermic stability and permit also to situate better their domain of a proper application. We observe on the thermogram of PTHF the presence of an exothermic accident between 200 and 280 °C. Centred in 259 °C attributed to the reticulation of polymeric chains. From this pick, the curve exhibits a descent that corresponds to the beginning of the decomposition of PTHF (Fig. 7).

3.3. Characterizations of nanocomposites of matrix PolyTHF

3.3.1. IR spectroscopy

The infra-red spectrum of organophile PTHF Mmt nanocomposites bring out the bands of absorption of PTHF and those associated with Mmt showed the presence of two organic/inorganic phases in the finished material without to state the nature of interactions between the two phases.

Fig. 8 represents the IR spectra of obtained nanocomposite for the different acids and shows that they are similar. The appearance of two bands of absorption bound by inorganic phase situated of 3622 and 3422 cm^{-1} due to the OH grouping vibrations of constitution of silicated skeleton and an OH physisorbed by clay.

The organic phase showed by the band situated in 2852 cm $^{-1}$ attributed to the vibrations of the binding C–H of methyl grouping and of 1680 cm^{-1} correspond to a carbonyl groping (C–O) of ester. The situated band of 1640 cm^{-1} is attributed to the deformation of absorbed water by the montmorillonite. The band of absorption corresponds to the presence of the ether function (C–O) (1113 cm^{-1}) is masked by the presence of the characteristic band of bindings Si–O has a strong intensity (1035 cm^{-1}).

We notice also the band of vibration of (Al–O) deformation that arises by a pick of 640 cm^{-1}.

3.3.2. X Diffraction and TEM

The infra-red spectroscopy has shown the presence of two organic and inorganic phases, with the confirmation of the polymerization of THF without to specify the type of interactions between the polymer and clay. Several types of nanocomposites could be obtained by the process of used synthesis.

- The inserted nanocomposites in which the interlayer of clay increase lightly by the insertion of polymer, the leaves face to face, are separated by the inferior distances of 30 . The leaves are inserted by the polymer chains and from the piles of similar size to that one of primary particle clay.
- The exfoliated nanocomposites in which the leaves are individualized and totally dispersed in the matrix. The leaves do not present more crystalline organization and the interlayer distance is upper than the one measured by diffraction of X-rays.
- These leaves or some nanoleaves are dispersed in the material. Very often the nanocomposites morphology results from the combination of the two last exfoliated structures.
- Ray et al. (Ray and Okamoto, 2003; Okamoto, 2004) propose the existence of inserted structure floccules, in which the inserted leaves unites, are flocculated because of the interaction between the boards of leaves.

The spectra of X-rays diffraction are realized for different mixing in order to evaluate the structural changes of the obtained composites in function of the nature of acid used to initiate the polymerization. We noticed that the DRX spectra of nanocomposites of the interlayer distance growth (d_{001}). This distance is variable to the nature of the used acid.

According to the obtained diffractograms for (NanoT1) the interlayer distance (d_{001}) is inferior to that of the organophile Mmt, we could not, therefore, conclude that the formation of nanocomposites in which the insertion of polymer takes place in the interfoliaire galleries. In other diffractograms, the obtained nanocomposite is confirmed by the interlayer (d_{001}) distances value which are upper than the one of the organophile Mmt (Fig. 9).

Its morphologies are, however, different: In the diffractograms of (NanoT2), (NanoT3), (NanoT4) and (NanoT5) we

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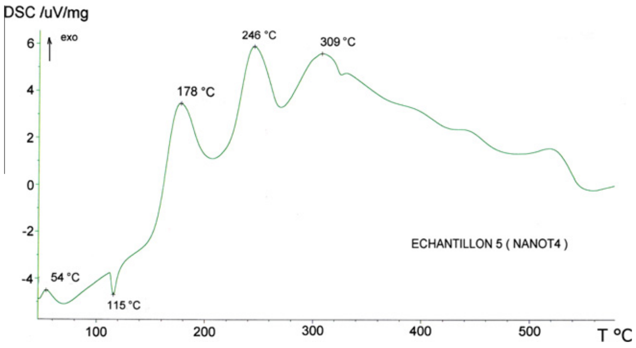

Figure 12 A DSC thermogram of PTHF–Mmt org (NanoT4) nanocomposite.

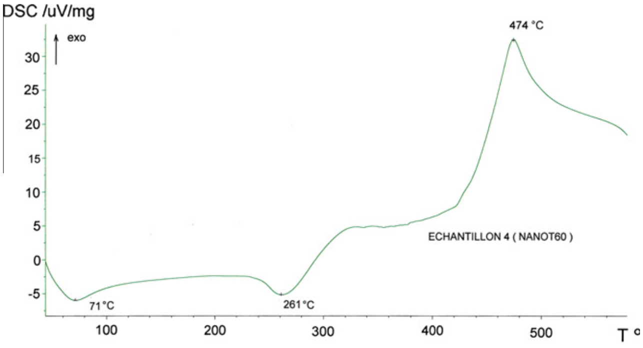

Figure 13 A PTHF–Mmt org (NanoT60) nanocomposite of DSC thermogram.

observe a respective interlayer distance of 22.6, 19.8, 23.5 and 22 ; we take in consideration the publication results in the bibliography we can say that the nanocomposites are inserted by the insertion of some strata of polymer (Yenice et al., 2009) in the interlayer space.

We notice in the diffractogram of (NanoT60) an important shifting of 1st pick of diffraction in relation to the one of the organophile Mmt, the (d_{001}) move always up to 24.9 ($2\theta = 3°$), according to the previously published results (Ray and Okamoto, 2003) we can say that the nanocomposite is a mixte exfoliated–intercalated of structure (Fig. 10 and Table 3).

The PTHF-clay nanocomposites obtained have also been analysed by Transmission electron microscopic (TEM) Phillips E391 with an accelerating voltage of 60 kV (Fig. 11). Regardless of the preparation method, any trace of remaining micron-sized clay aggregates could be detected throughout the studied samples.

Rather thin clay nanoplatelets proved randomly distributed in the PTHF matrix, as shown by finely dispersed nanolayers as observed from their edge side, that is, thin contrasted laments visible in Fig. 11 (as highlighted by black arrows).

3.4. The effect of the nature of the acid about the nanocomposites of thermic behaviours

3.4.1. The NanoT4 ($HClO_4$ (1 N)) a sample thermogram

The presence of nanocharges in a polymer matrix will have the consequences of the properties of material as in all biphased system. Moreover the incorporation of nanoleaves modified montmorillonite nanoleaves which accompanies the creation of an interphase between the matrix and leaf chemically modified.

We chose two samples which are the best intercalation and the different morphology according to this table to study their thermic behaviour.

In general nanoleaves ameliorate remarkably the thermic properties of the polymer thank to their dispersion in nanometric scale in the matrix.

We observe in this thermogram Fig. 12 an endothermic pick of 116 °C is associated with a departure of the physisorbed water, follow a second endothermic of 246 °C of the crystallization of HDTMAB.

The reticulation of the PTHF chains in the nanocomposites appear later towards 309 °C in relation to the same phenomenon in the virgin matrix because of the presence of clay which stabilize the material thermically. The last visible phenomenon about the thermogram is attributed to the decomposition of PolyTHF. It starts from 520 °C.

3.4.2. A NanoT60 ($C_4H_4O_4$ (1 N)) sample of thermogram

The first endothermic pick is 71.5 °C it is associated with a departure of the physisorbed water (Pandey et al., 2005). The presence of the endotherm of 261 °C is linked to the fusion of HDTMAB.

The reticulation of chains of the PTHF in the nanocomposite towards 474 °C is delayed in relation to the same phenomenon in the virgin matrix because of the thermic stability induced by the presence of clay in the material.

The last visible phenomenon about the thermogram is attributed to the decomposition of the PolyTHF, it starts towards 500 °C (Fig. 13).

The two nanocomposites observed are thermally more stable than the virgin PTHF. This growth of the thermic stability of nanocomposites clears itself by the barrier effect of the clay. At the same time the decomposition of the oxygen, and the molecules of gas of born of products diffuse more lightly broke in their polymeric matrix the graduation it then delayed (Yeh et al., 2004; Jordan et al., 2005).

4. Conclusion

The efficacy of organophile treatment of the clay is established by the diffraction of X-rays. The moving of the d_{001} of the Mmt Na^+ exchanged with the HDTMAB which moves from 12 to 20 Å and confirms the interaction of the carbonaceous chain in the galleries of the clay.

According to the XR diffractograms, we have obtained nanocomposites-polytétrahydrofuran-organophile montmorillonite of nanocomposites to different structure according to the used acid for starting the polymerization and according to the conditions of synthesis.

The infra-red spectra of elaborated nanocomposites that confirm the presence of the montmorillonite and the polymer in the obtained products. The bands of absorption of PTHF confirmed the polymerization.

The IR spectra of nanocomposites obtained for the different acids are similar, but the RX diffractograms show differences.

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According to the obtained results the maleic acid gives the best thermic resistance by obtaining intercalated–exfoliated nanocomposite presenting a $d_{001} = 24.9$ Å.

As a conclusion, the synthesis of PTHF–Mmt of nanocomposite is more influenced by the nature of the baiter of polymerization. The decomposition of these nanocomposites start at an upper temperature to that one of the pure PTHF and their thermic stabilities are relativity proportional with the intercalation type of polymer. Several ways could be explored so as to complete this study. At the same time, it is possible to ameliorate the interaction of the interface between nanocharge and matrix in order to promote the whole mechanic properties.

The perspectives which offer this work are numerous on the control of the structure-properties of organic/inorganic materials.

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