

## Fluorination of Algerian Montmorillonite Sodium by Cold Plasma and Its Effect on the Properties of PE-Based Composite

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### Abstract

*The present study consists of surface modification of industrial sodium montmorillonite (MT-Na) by cold plasma treatment. In order to increase its compatibility with polyethylene, a gas precursor, carbon tetrafluoride (CF<sub>4</sub>) is used in this physical process. The treated MT-Na is characterized by X-ray photoelectron spectroscopy. Prepared samples of LDPE/MT-Na and LDPE/MT-CF<sub>4</sub> mixtures are characterized by Fourier transform infrared spectroscopy (FTIR); scanning electron microscopy (SEM); differential scanning calorimetry (DSC); tensile and dynamic rheology tests.*

**Keywords:** cold plasma, fluorination, montmorillonite, polyethylene and nanocomposite.

### Introduction

Clays are environmentally friendly materials with a very high surface area and a high thermal and chemical stability. These clays consist of particles called tactoids of thickness 1-10 μm, composed of hundreds of platelets or laminates stacked by strong attraction forces. The cold plasma treatment method is of great importance because of it is non-polluting, which is not negligible for industrial manufacture, and its short reaction time [1]. This has been during the last decade at the origin of the increase of the use of this process in particular for the modification of nanostructures. It has been shown that after plasma treatment with different gases or monomers [2–5], nanoparticles acquire new surface properties. This surface modification induces a surface functionality that is designed to increase interactions with substrates of interest. Célini et al. [6] showed that the acetylene plasma treatment of laponite (LP-Na) leads to structural reconstruction, with the clay mineral becoming hydrophobic while the montmorillonite treated (MT-Na) becomes more hydrophilic. Krásny et al. [7] studied the effect of air plasma treatment on nano/micro modification of Kaolin particles on the physicochemical, mechanical and thermal properties of polyethylene composite. Valdrè et al. [8] studied the effect of different plasma gaseous environments (argon, air, water vapor and hydrogen) on the layer of vermiculite for the development of clays with increased properties for technological purposes and new applications. Şahin et al. [9] found that cold plasma treated bentonite (N<sub>2</sub>, Ar, and CO<sub>2</sub>) can be used more effectively to remove methylene blue from aqueous solutions. CF<sub>4</sub> plasma is considered a source of radicals (CF, CF<sub>2</sub>, CF<sub>3</sub>), F atoms and charged particles [10-16]. So the phase plasma makes it possible to functionalize by chemical grafting of CF, CF<sub>2</sub> and CF<sub>3</sub> [11]. However, very little work has been done on the fluorination of clay mineral surfaces. Trissaud and coworkers [17] is the only team that studied the effect of fluorination on various types of phyllosilicate minerals (lepidolite, muscovite, biotite and kaolinite). Their interest was to functionalize the surface of these materials, either by a reactive etching process involving fluoride species or by depositing a layer of carbon fluoride. Poncin-Epaillard et al. [18] described the modification of CF<sub>4</sub> plasma as the sum of two mechanisms, namely degradation and fluorination. These reactions appear to be competitive and parallel and the rates of degradation and fluorination are dependent on the treatment time. These two parameters seem to reach steady state after a certain reaction time since higher degrees of fluorination are not observed with longer reaction times.

Due to the plasma treatment, the dispersion of the nanoparticle and the interfacial adhesion to the polymeric matrix, have been improved, resulting in an increase in the mechanical properties of the nanocomposites [3, 19-20]. Plasma polymerization results in an ultra-polymeric coating deposited on the surface of the nanoparticles, which could significantly modify the surface properties of the nanoparticles [21].

Nanoparticles are considered as one of the main reinforcements of polymeric matrices and the promotion of new improved properties in these polymers, such as barrier properties (gas, vapor and moisture), flame resistant characteristics, and improved mechanical properties [22] without changing other important features such as transparency or density. Scaffaro et al. [23] improved the mechanical performance of poly [ethylene-co- (vinyl acetate)] (EVA) nanocomposite. For this purpose, the organically modified montmorillonite (Cloisite 15A) has undergone air plasma treatment to introduce polar entities in order to improve its affinity with the matrix.

The aim of this work is to modify the surface of industrial sodium montmorillonite (MT-Na) by a physical process (CF<sub>4</sub> cold plasma treatment) to increase its compatibility with a non-polar polymer such as polyethylene.

## **Experimental**

### **1. Materials**

Industrial sodium montmorillonite (MT-Na) provided by Sonatrach-Algeria, was used as received, and was only sifted with a sieve of 63 micron porosity. Carbon tetrafluoride CF<sub>4</sub> (high Purity, 99.95 %), was provided by Air Liquide. Low-density polyethylene (LDPE) used as matrix in this study, is a product of ENIP (Skikda, Algeria) with a density of 0.923g/cm<sup>3</sup> and a melt flow index of 1.2g/10min.

### **2. Plasma treatment**

The plasma treatment of clay is performed in a capacitively coupled radio frequency reactor designed for the treatment of powders. This treatment has been well described by Célini et al. [6] and Fatyeyeva et al. [24]. The excitation module is an RF generator at 13.56 MHz (Sairem 0 – 100W). A vibrating plate (180mm long, 120mm wide and 14mm high) guarantees a homogeneous mixture of the clay mineral during plasma treatment. Various vibration frequencies (mechanical agitation) (from 0 to 270 a.u. (arbitrary unit)) can be applied during the treatment of clay minerals. The mineral sample (0.5g) was spread over the plate. Plasma fluorination on particulate matter was studied as a function of time (t = 60s, 90s, and 180s) using two plasma powers (P = 50W and P = 80W) at a flow Q of 30sccm (standard centimeter cube per minute) and a vibrational frequency of 80.

### **3. Composite preparation**

The mixtures were prepared from low density polyethylene (LDPE), untreated clay and CF<sub>4</sub> plasma treated clay in a proportion LDPE/clay: 97/3 (% mass). A double screw mini-extruder (at the temperature of 160°C with a speed of screw rotation of 40 rpm and during an 8min cycle) has been used to mix the samples.

### **4. Characterization Methods**

X-ray photoelectron spectroscopy (XPS) consists of analyzing the kinetic energy of the emitted electrons of the material under the effect of irradiation by the X-photons used. The spectrometer used is Axis Nova (Kratos) which is equipped with an X-ray source of aluminum.

IR spectra were recorded in transmission mode (composite) and in attenuated total reflection (ATR) technique (clay), within the range of 4000-400cm<sup>-1</sup>, using the FTIR Bruker spectrometer Vertex 70V.

Scanning electron microscopy (SEM) was performed using with a microscope JEOL, JSM 6510 LV (Europe). A variable voltage microscope of 0.3-30kV, which is equipped with an EDS microanalysis system, including the Oxford instrument X-Max type detector. The metallization with gold was performed in argon atmosphere at 8Pa using a JFC-1300 sputter coater with a current of 30mA for 40s.

The tensile tests were carried out at room temperature on a universal mechanical testing machine "ZWICK/ROELL Z010" at a speed of 50mm/min. The test specimens are prepared according to the ISO/DIS 527specifications.

Differential Scanning thermal analysis (DSC) was performed on a DSC Q100 mark apparatus. The mass of the sample in the capsule is between 5 and 7 milligrams. The scans were carried out at a heating rate of 10°C/min in a temperature range of -80°C to 150°C.

The dynamic rheology measurements were studied using a Thermal Analysis RS100rheometer equipped with a 25mm diameter stainless steel parallel disc at 1mm air gap. All measurements were made in the linear viscoelasticity domain at a temperature of 140°C.

**Results and discussion**

**1. CF<sub>4</sub> plasma treatment of MT-Na**

X-ray photoelectron spectroscopy (XPS) is a technique for analyzing the surface of a material (~ 100A°). It allows us to determine the chemical nature of the various elements present as well as their proportions in each sample. The results of our analysis are shown in Tables 1-2. The quantification of the survey spectrum of untreated MT-Na, shows the presence of a very small amount of fluorine (ca. 0.83%) at 685.3eV [25] this is due to an impurity contained in MT-Na.

**1.1. Influence of MT-Na processing RF power by CF<sub>4</sub> plasma**

The processing of the XPS of MT-CF<sub>4</sub> (table 1) shows that low and close values in the atomic percentage of fluorine are obtained for a processing time of 60s at RF powers of 50W and 80W. It can be said, in this case, that the high pressures have no effect on the treatment. Moreover, the low value of the measured fluorine content is an indication of the difficulty of grafting fluorinated groups on the powder which is due to the nonhomogeneous distribution of clay on the substrate holder.

**Table1: Results of the XPS analysis of untreated clay and CF<sub>4</sub> plasma treated clay (t = 1min, Q = 30sccm and f = 80)**

		P (W)	0	50	80
<b>O1s</b>	% Atomic		55.33	53.24	54.17
	Position (eV)		532.4	532.4	532.4
<b>Si2p</b>	% Atomic		23.35	23.35	24.42
	Position (eV)		103.2	103.2	103.2
<b>Al2p</b>	% Atomic		9.21	8.84	8.42
	Position (eV)		75	75	75
<b>Mg2p</b>	% Atomic		-	2.01	2.10
	Position (eV)		-	86	86
<b>Na1s</b>	% Atomic		2.46	2.49	2.91
	Position (eV)		1072	1072	1072
<b>F1s</b>	% Atomic		0.81	1.69	1.96
	Position (eV)		685.3	685.3	685.3
<b>C1s</b>	% Atomic		8.36	8.38	5.83
	Position (eV)		285	285	285

**1.2. Influence of MT-Na processing time by CF<sub>4</sub> plasma**

According to table 2, the absence of the fluorine peak is noted for CF<sub>4</sub> plasma processing times beyond 60s. Thus, the increase in processing time is not in favor of the fixation of fluorinated groups which may be due to the degrading effect of CF<sub>4</sub>. In fact, according to Poncin-Epaillard et al. [17], the degrading effect of CF<sub>4</sub> increases with increased plasma (treatment time, power) due to the reactivity of fluorine species. So, it seems that a time of 60s and a RF power of 80W, are the conditions of CF<sub>4</sub> plasma treatment which favors little the fixation of the fluorinated groups and, thus generates, the hydrophobic character of MT-Na.

**Table 2 Results of the XPS analysis of CF<sub>4</sub> plasma-treated MT-Na (P = 80W, Q = 30sccm, and f = 80)**

t (s)		0	60	90	180
<b>O1s</b>	Atomic %	55.33	54.17	48.64	49.79
	Position (eV)	532.4	532.4	532.4	532.4
<b>Si2p</b>	Atomic %	23.83	24.42	22.86	24.23
	Position (eV)	103.2	103.2	103.2	103.2
<b>Al2p</b>	Atomic %	9.21	8.42	8.67	9.11
	Position (eV)	75	75	75	75
<b>Mg2p</b>	Atomic %	-	2.10	-	2.24
	Position (eV)	-	86	-	86
<b>Na1s</b>	Atomic %	2.46	2.91	1.38	2.37
	Position (eV)	1072	1072	1072	1072
<b>F1s</b>	Atomic %	0.81	1.96	-	-
	Position (eV)	685.3	685.3	-	-
<b>C1s</b>	Atomic %	8.36	5.83	17.94	12.21
	Position (eV)	285	285	285	285

**Table 3 Band Assignment of the FTIR spectrum of the LDPE [26].**

Band (cm <sup>-1</sup> )	Assignment
2928	Asymmetrical stretching vibration of CH <sub>2</sub>
2858	Symmetrical stretching vibration of CH <sub>2</sub>
1458	Bending vibration in the plan of CH <sub>2</sub>
720	Bending vibration out the plan of CH <sub>2</sub>

**Table 4 Band Assignment of the FTIR spectra of the MT-Na [27, 28, 29].**

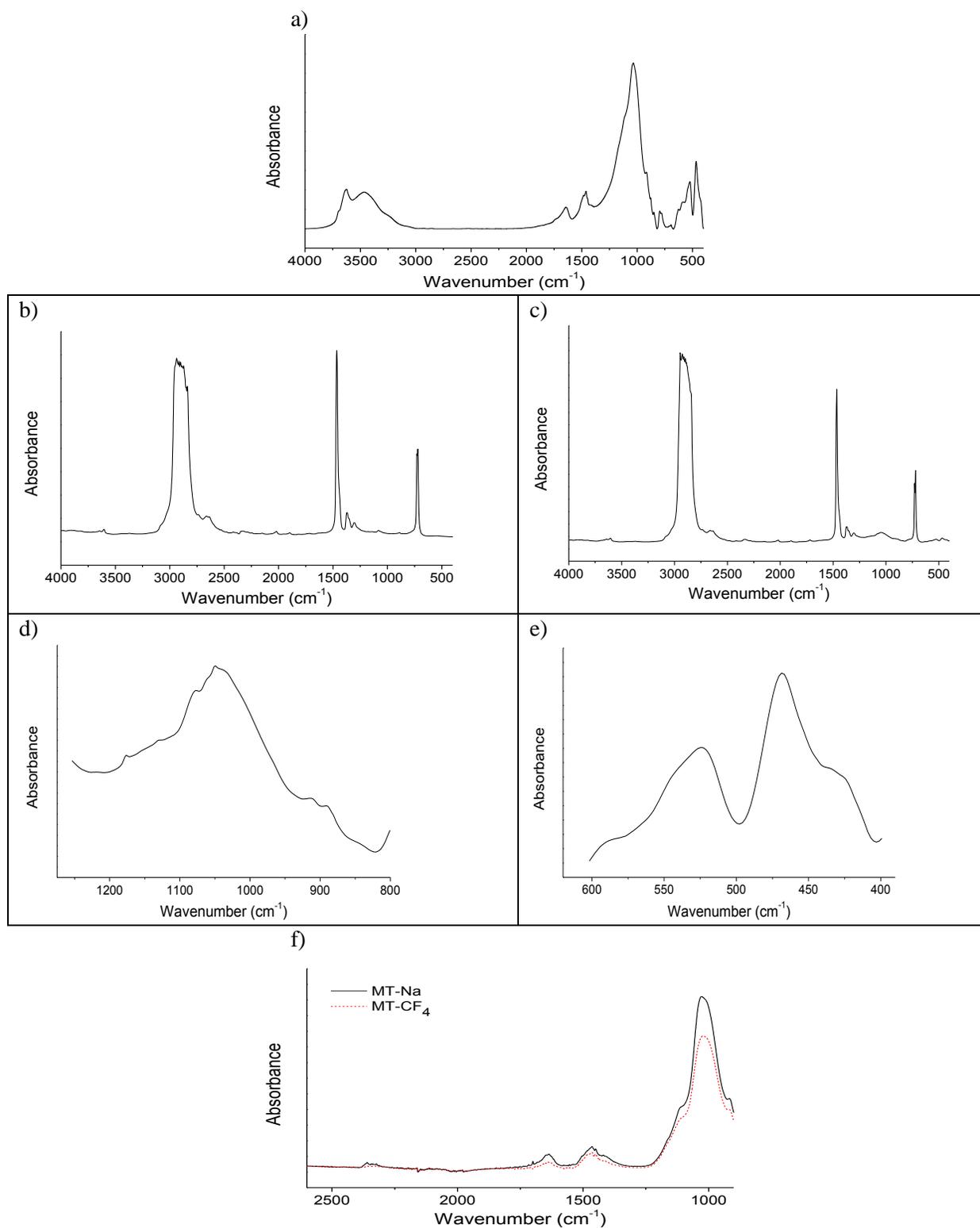
Band (cm <sup>-1</sup> )	Assignment
3628	Stretching vibration of OH in Al <sub>2</sub> OH of octahedral sheet of silicates
3433	Stretching vibration of adsorbed water bond
1635	Bending vibration of adsorbed water bond
1468	Stretching vibration of C-C
1028	Stretching vibration of Si-O-Si bond in tetrahedral sheets
917	Bending vibration of OH in Al <sub>2</sub> OH of octahedral sheets
525	Bending vibration of Si-O-Al bond
455	Bending vibration of Si-O-Si bond

## 2. Properties of mixtures

### 2.1. Chemical and morphological characterization

#### -Fourier Transform IR spectroscopy

In addition to characteristic bands of the LDPE matrix (reported in figure 1b and summarized in table 3 ) the spectrum of the LDPE/MT-Na mixture (Figure 1c) show new bands at 1028cm<sup>-1</sup>, 525cm<sup>-1</sup>, and 455cm<sup>-1</sup> respectively associated with the Si-O-Si stretching vibration of the silicate network, bending vibrations of Si-O-Al and the Si-O-Si, as presented in figure 1a and specified in table 4 (which summarizes the characteristic vibration modes of this type of 2:1 layered silicates). This confirms the incorporation of the silicate particles into the LDPE matrix. Comparing the bands between 1000 and 2600 (figure 1g), we note that there is no additional band on the CF<sub>4</sub> plasma-treated clay. Indeed, this technique does not seem sensitive enough to detect fluorine on the surface modified by CF<sub>4</sub> plasma.

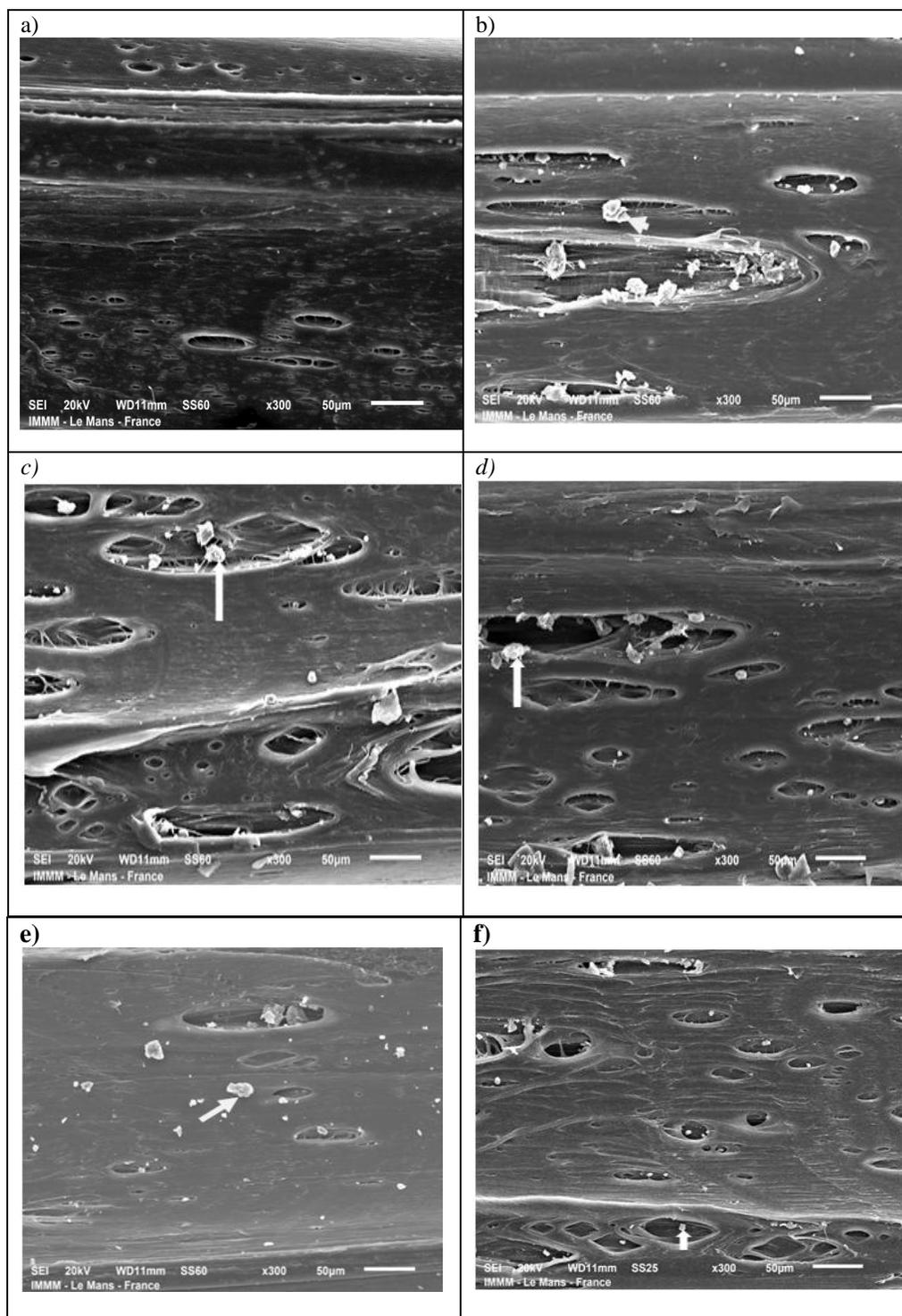


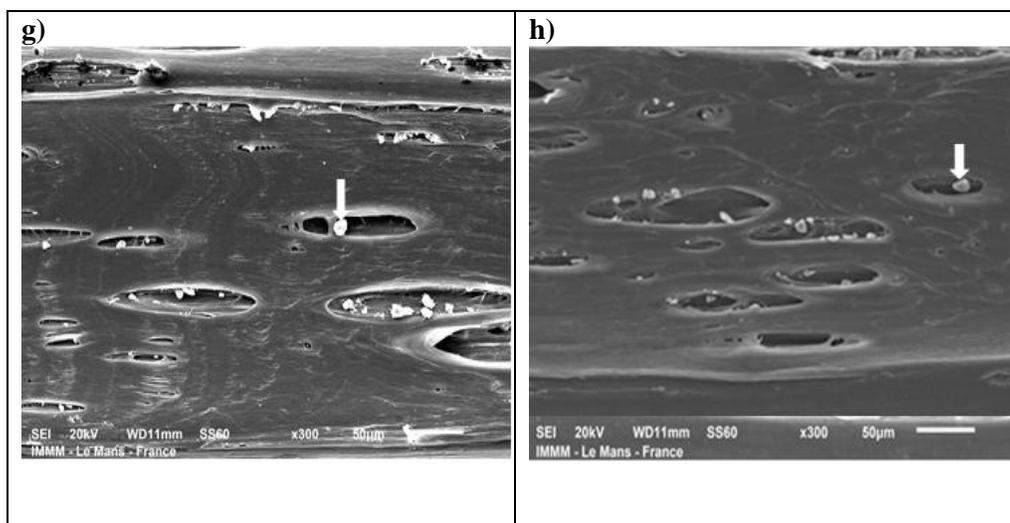
**Figure 1. FTIR spectra a) MT-Na, b) LDPE, c) LDPE-MT-Na and band absorption bond d) Si-O-Si at 1028cm<sup>-1</sup>, e) Si-O-Si at 525cm<sup>-1</sup> and Si-O-Al at 455cm<sup>-1</sup> and f) MT-Na and MT-CF<sub>4</sub> in the range 2500 - 1000cm<sup>-1</sup>.**

#### **-Scanning electron microscopy (SEM)**

Scanning electron microscopy analysis was performed on the fractured part of the tensile test samples.

The SEM images (Figure 2) show the presence of clay in the LDPE matrix as small particles and agglomerates, the size of which varies between 2 $\mu$ m and 40 $\mu$ m. It is noted that for samples treated with CF<sub>4</sub> during 60s at RF power 80W, give a better dispersion of the clay. This is translated by a reduction in the number of agglomerates as well as their size.

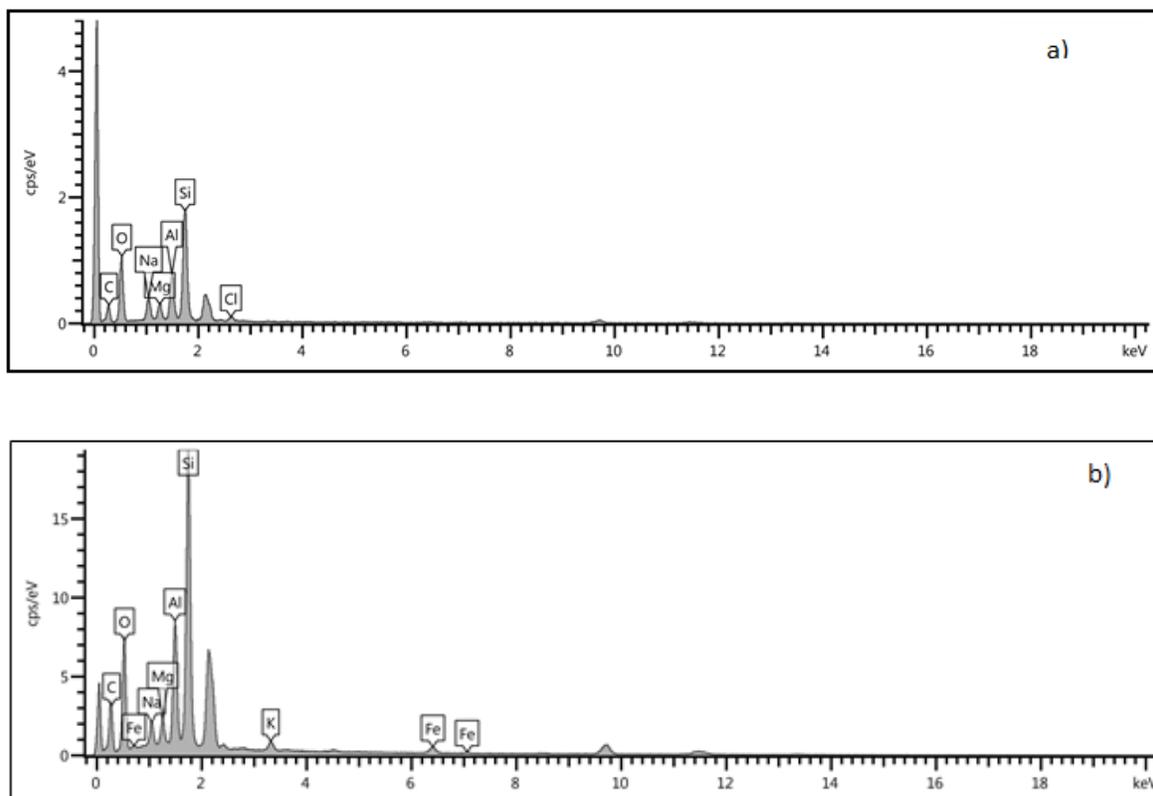




**Figure 2. SEM micrographs for : a) LDPE, b) LDPE/MT-Na, c) LDPE/MT-CF4-60s50W, d) LDPE/MT-CF4-90s50W, e) LDPE/MT-CF4-180s50W, f) LDPE/MT-CF4-60s80W, g) LDPE/MT-CF4-90s80W, and h) LDPE/MT-CF4-180s80W.**

#### -Energy dispersive X-ray spectroscopy (EDS)

Through the EDS spectra (Figure 3) we observe the presence of the main constituents of MT-Na, i.e. oxygen, silicon, aluminum, magnesium and sodium and impurities such as iron, carbon and chlorine. This allows us to confirm the presence of clay observed on the SEM images shown above.



**Figure 3. EDS spectra a) LDPE/MT-Na and b) LDPE/MT-CF4-60s80W**

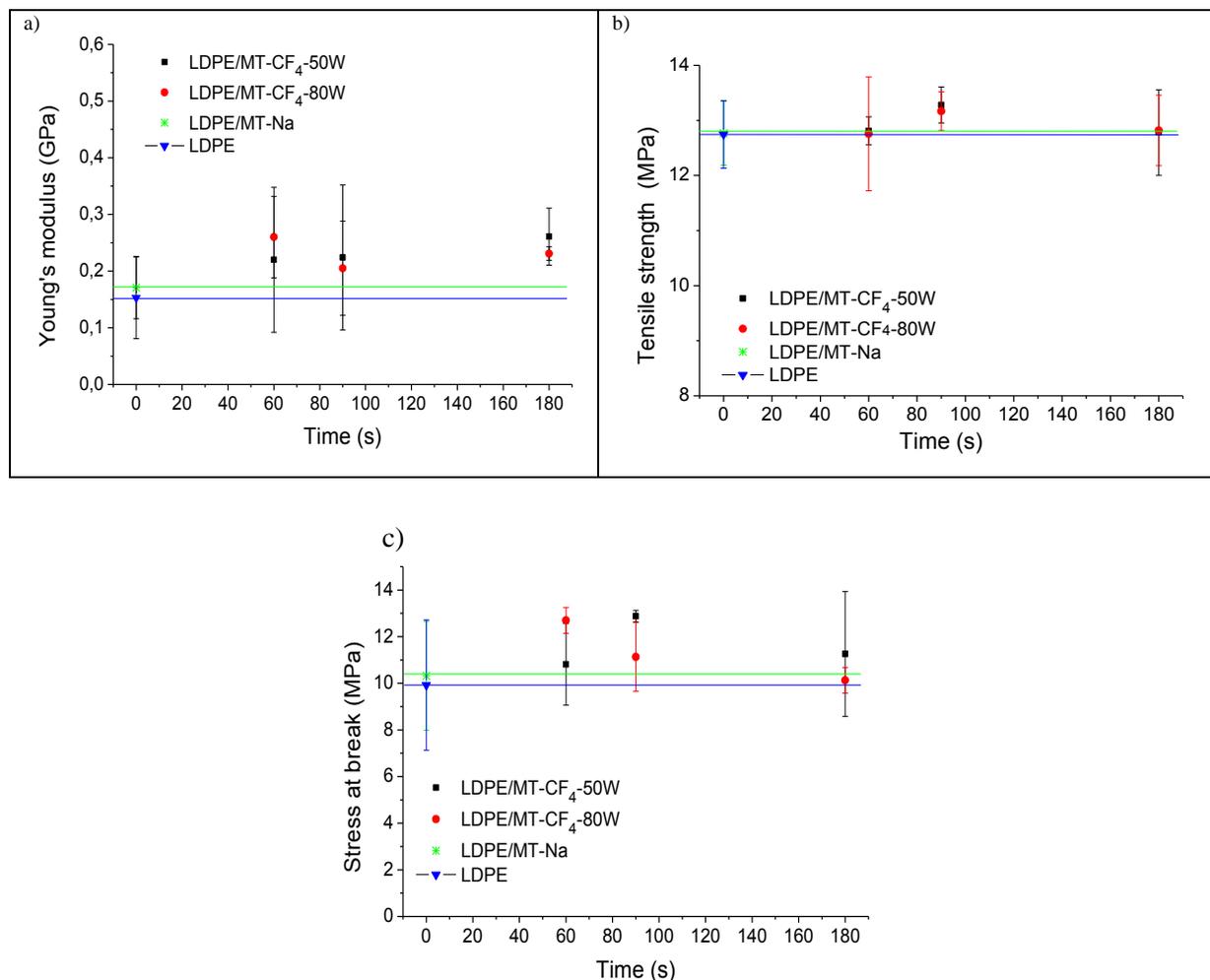
## 2.2. Tensile test

The results of the tensile test (Young modulus (E), tensile stress ( $\sigma_M$ ) and stress at break ( $\sigma_r$ ) at different CF<sub>4</sub> plasma processing times, are presented in table 5. According to these results, the sample treated with plasma CF<sub>4</sub> during 60s to the RF power of 80W shows the best mechanical properties.

**Table 5 Results of the tensile test**

Sample	E (GPa)	$\sigma_M$ (MPa)	$\sigma_r$ (MPa)
LDPE	0.153±0.07	12.741±0.61	9.92±2.79
LDPE/MT-Na	0.171±0.05	12.768±0.58	10.324±2.33
LDPE/MT-CF <sub>4</sub> -60s50W	0.22±0.127	12.81±0.22	10.813±1.75
LDPE/MT-CF <sub>4</sub> -90s50W	0.224±0.13	13.28±0.32	12.875±0.25
LDPE/MT-CF <sub>4</sub> -180s50W	0.261±0.05	12.78±0.78	11.26±2.68
LDPE/MT-CF <sub>4</sub> -60s80W	0.26±0.07	12.7565±1.03	12.697±0.55
LDPE/MT-CF <sub>4</sub> -90s80W	0.205±0.08	13.168±0.35	11.132±1.48
LDPE/MT-CF <sub>4</sub> -180s80W	0.231±0.01	12.817±0.64	10.13± 0.55

According to figure 4, there is an increase of the stress at break for the processing time of 60s at the RP power of 80W and 90s at the RF power of 50W, and a small increase in the tensile strength for the processing time of 90s at the RF power of 50W. This improvement could be associated with the existence of some interfacial adhesion between the matrix and clay which promotes a good stress transfer [30].



**Figure 4. Variation of the tensile test as a function of processing time, a) Young's modulus , b) tensile strength stress and c) stress at break.**

The increase in Young's modulus (Figure 4a) is due to the positive effect of the presence of clay. Indeed, the incorporation of rigid particles of clay into a matrix improves the modulus of the composite which is due to a restriction in the movement of polymeric chains [31]. An optimum value was obtained for a processing time of 60s to the RF power of 80W. This is explained by the hydrophobic character of the clay which has more affinity with the matrix following the  $CF_4$  plasma treatment which is well shown by the results of the XPS analysis.

### 2.3. Thermal properties

The thermograms obtained during the thermal analysis by DSC, are shown in figures (5a and 5b). Various results are extracted and summarized in table 6. Melting and crystallization temperatures show practically no variation. The variation of crystallinity as a function of processing time, is illustrated in Figure 6. There is a decrease in this characteristic for 80W treated samples, whereas an inverse behavior is observed for samples treated with 50W. The decrease in crystallinity is attributed to a high interfacial surface and also to a good adhesion between LDPE and Clay [32]. Therefore, the hydrophobic character of the clay treated with  $CF_4$ , improved its affinity with the matrix.

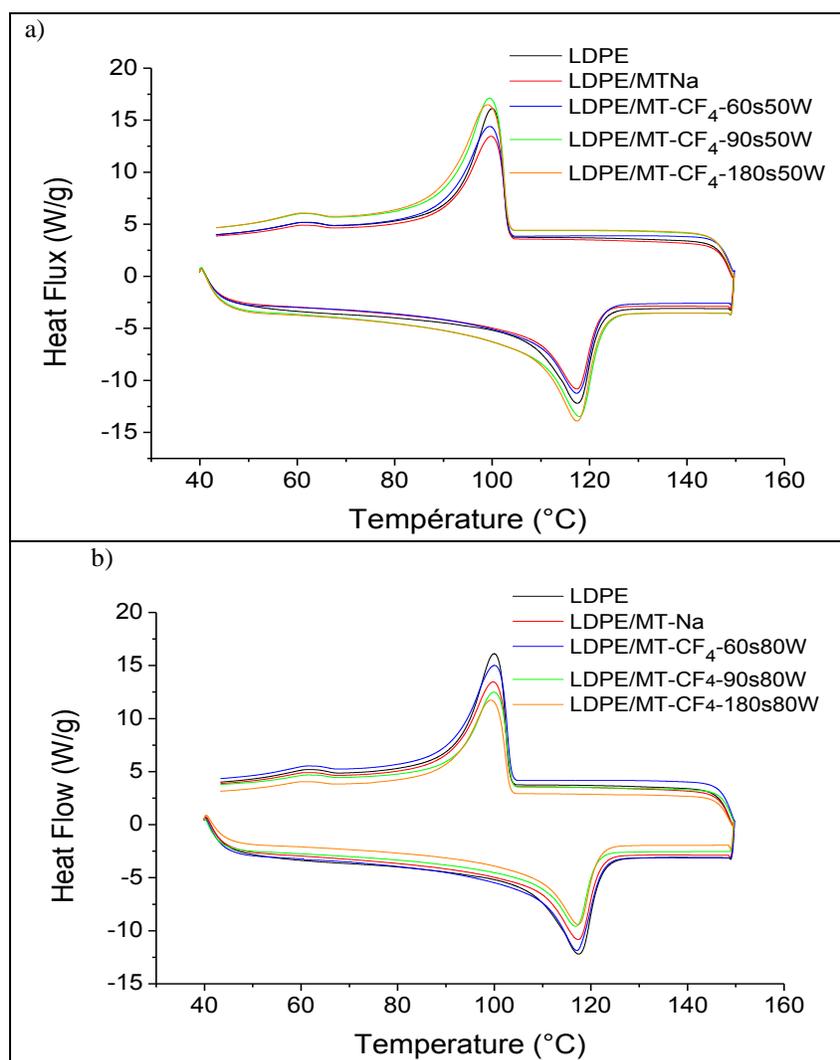
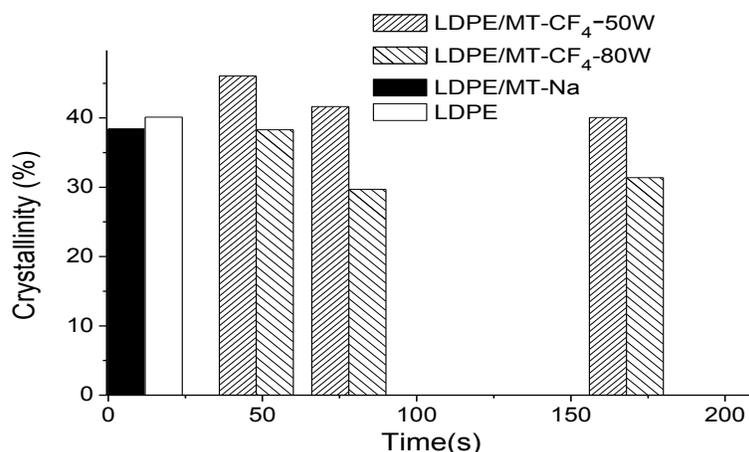


Figure 5. DSC Thermograms a) LDPE, LDPE/MT-Na and LDPE/MT-CF<sub>4</sub> treated at 50W and b) LDPE, LDPE/MT-Na and LDPE/MT-CF<sub>4</sub> treated at 80W.

**Table 6 Results of the DSC analysis**

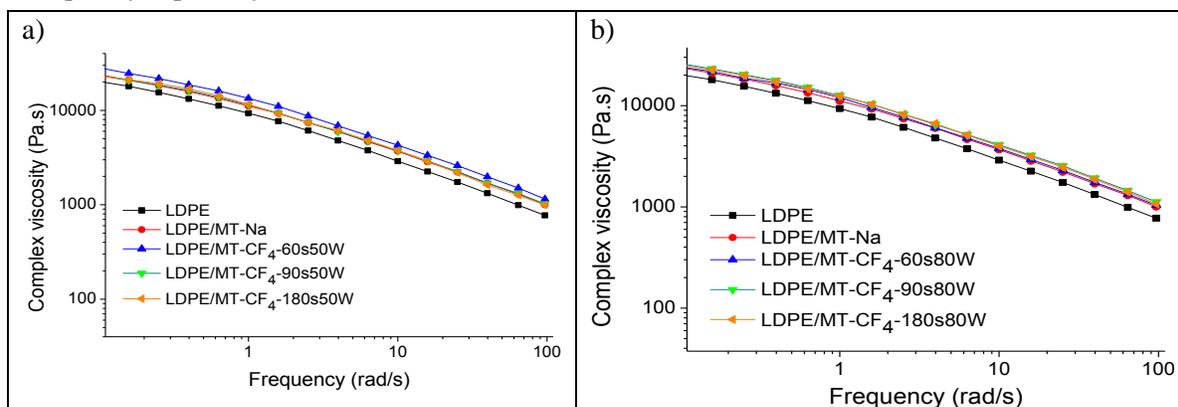
Sample	$T_f$ (°C)	$T_c$ (°C)	$H_f$ (J/g)	$H_c$ (J/g)	$X_c$ (%)
LDPE	117.56	100.11	117.9	94.35	40.12
LDPE/MT-Na	117.39	99.87	112.5	84.33	38.39
LDPE/CF <sub>4</sub> -60s50W	117.27	99.66	135	101.5	46.07
LDPE/CF <sub>4</sub> -90s50W	117.91	99.61	122.9	92.91	41.64
LDPE/CF <sub>4</sub> -180s50W	117.39	99.25	120.9	93.99	40.06
LDPE/CF <sub>4</sub> -60s80W	117.11	100.17	112.2	88.93	38.29
LDPE/CF <sub>4</sub> -90s80W	116.96	100.11	87.00	68.52	29.69
LDPE/CF <sub>4</sub> -180s80W	117.33	99.40	91.94	71.54	31.38

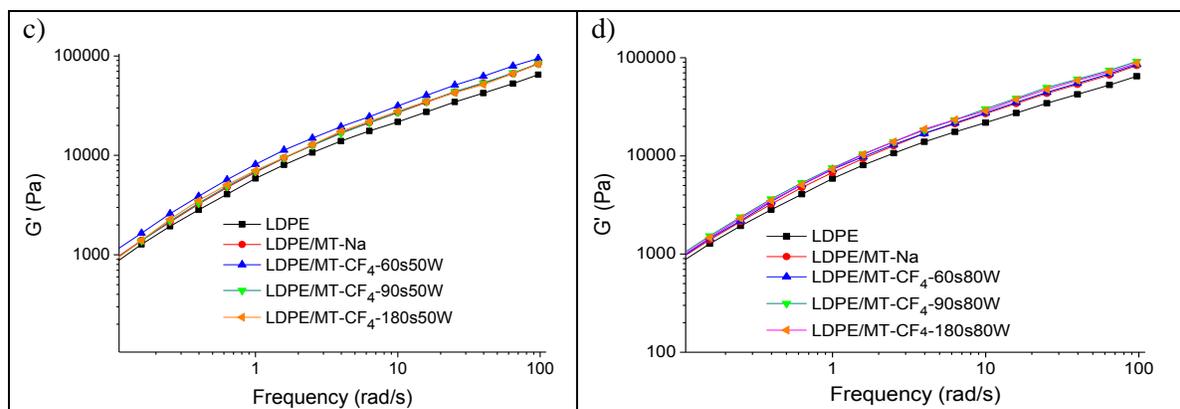
**Figure 6. Variation in crystallinity as a function of processing time**

#### 2.4. Rheological properties

Rheology is a powerful tool to obtain an integrated image of the materials nanocomposites seen that it provides information on the influence of nanofillers on the rate of local deformation of the polymer and also on the orientation and/or exfoliation, and their Interactions.

The rheological analysis of the different mixtures (Figure 7a to 7d) based on MT-Na and CF<sub>4</sub> treated clay at different processing times and at the RF powers 50W and 80W, shows no variation neither in the complex viscosity ( $\eta^*$ ) nor in storage modulus ( $G'$ ) compared to the untreated sample. This is due to the low amount used of clay (3% mass); in fact, the increase in the amount of charge induces an increase of shear storage modulus in the low frequency especially visible for 5 and 10% of loads [33].





**Figure 7. Frequency dependence of the complex viscosity ( $\eta^*$ ) and storage modulus ( $G'$ ) as a function of processing time.**

### Conclusion

In this work, the study of the effect of  $\text{CF}_4$  cold plasma treatment on the surface properties of Montmorillonite (MT-Na) used as a charge for the preparation of composites based on polyethylene (LDPE) was done. The effect of treatment time and the RF power on the physical-chemical, mechanical, thermal and rheological properties of composites, was also studied. X-ray photoelectron spectroscopy (XPS) revealed, that short  $\text{CF}_4$  plasma processing times (60 s) favor the fixation of fluorinated groups on clay particles, which gives them an hydrophobic character. Fourier transform infrared spectroscopy (FTIR) and Energy dispersive X spectroscopy (EDS) confirmed the incorporation of silicate particles into the LDPE matrix. The morphological study by electron microscopy (SEM) showed that low 60s processing times of MT-Na by  $\text{CF}_4$  plasma improves the dispersion of the clay in the LDPE matrix.

An improvement in the mechanical properties of the loaded polyethylene composites treated during 60s to the 80W RF power, is observed compared with the untreated loaded polymer and the Virgin polymer. The thermal analysis by DSC showed a decrease in crystallinity in the case of samples treated with 80W which is attributed to a high interfacial surface and also to a good adhesion between LDPE and clay. We found an absence of any variation in rheological properties of the mixtures with treated clay by comparison to the untreated one.

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