



Research Article

# Ultrasound Assisted Synthesis of Polylimonene and Organomodified-clay Nanocomposites: A Structural, Morphological and Thermal Properties

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## Abstract

Polylimonene-clay nanocomposites (PLM-Mag 2, 3, 6 and 10% by weight of clay) were prepared by mixing Maghnite-CTA<sup>+</sup> (Mag-CTA<sup>+</sup>) and polylimonene (PLM) in solution using ultrasonic irradiation. The catalyst preparation method were studied in order to determine and evaluate their structural, morphological and thermal properties. The Mag-CTA<sup>+</sup> is an organophylic montmorillonite silicate clay prepared through a direct exchange process, using green natural clay of Maghnia (west of Algeria) called Maghnite. The Algerian clay was modified by ultrasonic-assisted method using cetyltrimethylammonium bromide (CTAB) in which they used as green nano-reinforcing filler. Polylimonene was obtained by the polymerization of limonene, using Mag-H<sup>+</sup> as a catalyst. The morphology of the obtained nanocomposites was studied by X-ray diffraction (XRD), scanning electronic microscopy (SEM), transmission electronic microscopy (TEM) and infrared spectroscopy (FT-IR). Thermogravimetric analysis (TGA) shows that the nanocomposites have a high degradation temperature (200–250 °C) compared with the pure polylimonene (140 °C). The analyses confirmed the chemical modification of montmorillonite layers and their uniformly dispersion in the polylimonene matrix. Exfoliated structures were obtained for low amounts of clay (2 and 3% by weight), while intercalated structures and immiscible regions were detected for high amounts of clay (6 and 10% by weight). Copyright © 2020 BCREC Group. All rights reserved

**Keywords:** Ultrasound; Polylimonene; Nanocomposites; Organo-modified clay; Polymer/clay

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## 1. Introduction

In the last decades, a growing interest is fo-

cused on a new class of materials, reinforced by nanoscale particles, called nanocomposites. Interest in these new materials was initiated by Toyota researchers in the early 1990s. In fact, by dispersing clays in polyamide-6 by in situ

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polymerization, they showed a significant increase in dimensional stability [1]. These results have been the precursor to new perspectives for polymer matrix nanocomposites in many scientific fields [2]. In recent years, nanocomposites based on toxic polymers have been replaced by others based on green materials. The use of a polymer matrix by adding a well-defined percentage of clay as reinforcement leads to the improvement of the physicochemical properties of the resulting nanocomposites such as high modulus, increased heat resistance, adhesion and barrier gas properties, flammability, and increased biodegradability of biodegradable polymers [3,4]. Based on the interaction strength of the modified polymer/clay, two different types of nanocomposites structures can be synthesized, intercalated and exfoliated nanocomposites. The synthesis of nanocomposites can be done by different methods such as in-situ polymerization, solution blending of polymer and other methods [5].

Limonene is a monocyclic terpene found in many essential oils extracted from citrus zest [6]. The first polymerization of terpenes was carried out in 1798, when Bishop Watson added a drop of sulfuric acid to produce a sticky resin [7]. The copolymerization of limonene with other monomers, such as: styrene was also attempted using azobisisobutyronitrile (AIBN) as a radical catalyst [8]. However, at that time, the researchers could not distinguish the interesting properties of this material, which further delayed its 50 year study. In 1950, William Roberts studied the cationic polymerization of many terpenes such as limonene,  $\alpha$ -pinene and  $\beta$ -pinene with Friedel-Crafts catalysts, for example  $\text{SnCl}_4$  and  $\text{AlBr}_3$  [9]. By adding less than 1% of catalyst in toluene, William Roberts produces a solid  $\beta$ -pinene polymer with a low molecular weight of about 1500 g/mol. The degree of polymerization of  $\beta$ -pinene, although very low, is higher than that of the two other monomers (limonene,  $\alpha$ -pinene) [10,11]. Limonene has been widely used in a wide range of products such as cosmetics, as food additives, medicine and even as a green solvent [12].

The use of ultrasound for the preparation of nanocomposites based on polymer and clay in solution is very interesting. This method of synthesis was used to reduce the reaction time and also to increase the dispersion of nano-fillers in polymer matrix with most of them focusing to exfoliate the packed layers of clay [13–17]. The ultrasonification induces acoustic stream and cavitation bubbles that subsequently undergo an implosion process resulting in a consequent

release of heat and energy leading afterwards a highly well dispersed reaction medium [18], the use of ultrasound has also an impact on the morphology of the prepared nanocomposites especially in dispersion like in-situ polymerization methods [19]. For these reasons, several nanocomposites based on polymers and clay was prepared under ultrasound-assisted method.

By examining the literature, we find that the use of natural clay as nanoreinfort in the synthesis of green-nanocomposites based on polylimonene and clay is practically nonexistent. The main goal of this work is to use an organo-modified montmorillonite clay called Maghnite-CTA<sup>+</sup> (Mag-CTA<sup>+</sup>) as a new nano-reinforcing filler in order to improve both thermal and mechanical properties of polylimonene, also, to prepare green-nanocomposites out of green raw materials (limonene and clay). In previously published work, we have shown the advantage of applying this type of nanoreinfort in several nanocomposites synthesis [20]. It is preferred for its many advantages such as a very low purchase price compared to other nano-reinforcing fillers.

## 2. Materials and Methods

### 2.1 Materials

In this work we have used (R)-(+)-Limonene (97%), methanol ( $\text{CH}_3\text{OH}$ , 99.9%), Dichloromethane ( $\text{CH}_2\text{Cl}_2$ , 99.8%), cetyltrimethylammonium bromide (CTAB), sodium chloride ( $\text{NaCl}$ ) and sulphuric acid ( $\text{H}_2\text{SO}_4$ ) are supplied by Sigma Aldrich and used as received. Maghnite (Algerian montmorillonite) is supplied in the raw state by ENOF Bental Spa of the National Company of Nonferrous Mining Products, Maghnia Unit (Algeria). The ultrasound instrument used for the preparation of Mag-CTA<sup>+</sup> and nanocomposites consists of a jacketed glass vessel provided with ultrasonic horn (13.6 mm diameter made of Titanium alloy Ti-6Al-4V non-replaceable tip) equipped with a Sonics VC-750 Vibra6 Cell generator.

### 2.2 Characterizations of Catalyst

XRD diffraction patterns using Bruker AXS D8 diffractometer ( $\text{Cu-K}\alpha$  radiation). The functional groups of the modified clay and its nanocomposites were analyzed by infrared spectroscopy FT-IR in the range of 4000–360  $\text{cm}^{-1}$  using BRUKER ALPHA Diamond-ATR. Molar Masses of polylimonene were studied by SEC analyses using a GPC-PL120 apparatus,  $\text{CH}_2\text{Cl}_2$  (1.0 mL/min) as the mobile phase at

27.5 °C and Polystyrene standards were used for column calibration. Thermal properties were analyzed by thermogravimetric analysis (TGA) using PerkinElmer STA 6000 under air and nitrogen in the temperature range 30–700 °C with a heating rate of 20 °C/min. The surface morphology of the modified clay and its nanocomposites were observed by FEG-SEM on a JEOL 7001F electron microscopy and Transmission electron micrographs were performed on a Hitachi 8100.

### 2.3 Preparation of Maghnite-H<sup>+</sup> (Mag-H<sup>+</sup>)

Mag-H<sup>+</sup> is prepared according to the process reported in our previous study [21,22]. Mag-H<sup>+</sup> is activated with a sulfuric acid solution to give a Maghnite exchanged with protons. In an Erlenmeyer flask, crushed raw-Mag (20 g) is dispersed in a volume of distilled water (120 mL). The mixture is stirred 2 h at room temperature. Then, a solution of sulfuric acid (0.25 M) is added. The solution thus obtained is maintained for two days under stirring. The mineral is filtered off and washed several times with distilled water up to pH 7. After filtration, Mag-H<sup>+</sup> is dried in an oven for 24 h, at 105 °C and then crushed. Its structure is established by FT-IR and XRD.

**Table 1.** Effect of the amount of Mag-H<sup>+</sup> on the Mn of PLM.

Mag-H <sup>+</sup> (wt%)	Mn (g/mol)
2	360
4	513
5	625
10	1360
15	1320
20	1290
25	1192

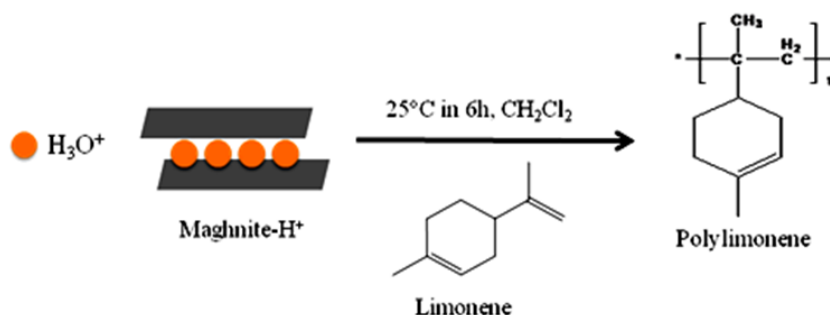
### 2.4 Preparation of Mag-Na<sup>+</sup> and Mag-CTA<sup>+</sup>

Mag-Na<sup>+</sup> was prepared according to the protocol described by Belbachir *et al.* [23]. The raw-Mag supplied by Bental Spa, is crushed and finely sieved, the activation of Maghnite by sodium was carried out using 1 L of NaCl solution (1 M) and 20 g of raw-Mag (2% by weight), the latter is mixed for 24 h at room temperature, finally the Maghnite was washed several times with distilled water.

The Mag-CTA<sup>+</sup> activation were carried out by ultrasound during 1 h [19]. Firstly 10 g of Mag-Na<sup>+</sup> is placed in a 1 L Erlenmeyer flask with the chosen concentration (1 CEC). At the end of the exchange process, the suspension is filtered and then washed several times with distilled water. Finally the solid obtained is dried at 105 °C during 24 h and ground. The structure of organophylic clay is confirmed by FT-IR and XRD analysis and their morphological properties are studied by SEM and TEM analysis.

### 2.5 Synthesis of Polylimonene (PLM)

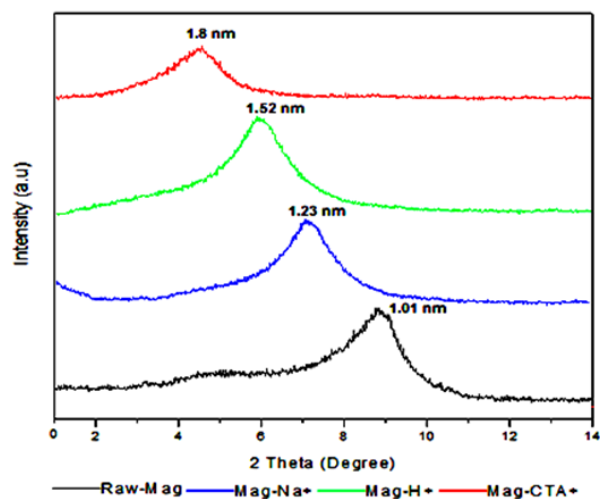
The polymerization of limonene is carried out according to the protocol described by Dardar *et al.* [24], in solution and in bulk using Mag-H<sup>+</sup> as catalyst. In a flask containing 2 g (0.01 mol) of limonene, we added an amount of 10% in weight of Mag-H<sup>+</sup> which is previously dried for 30 minutes in the oven at 105 °C. The mixture is stirred for 6 h at room temperature (25 °C). Table 1 summarizes the effect of the amount of Mag-H<sup>+</sup> on the Mn of the obtained polymer (PLM), using various amount of Mag-H<sup>+</sup> (2, 4, 5, 10, 15, 20 and 25 % by weight). The results of Table 1 show that 10 % by weight of Mag-H<sup>+</sup> seems to limit the increase of molar masses (Mn = 1360 g/mol). After 6 h, the reaction mixture is dissolved in CH<sub>2</sub>Cl<sub>2</sub>, filtered and precipitated in cold methanol (CH<sub>3</sub>OH) then dried in vacuum overnight. The polymerization reaction of limonene is described in Scheme 1.



**Scheme 1.** Polymerization of Limonene catalyzed by Mag-H<sup>+</sup>.

### 2.6 Synthesis of Nanocomposites Polylimonene/Clay (PLM-Mag)

The synthesis of PLM-Mag nanocomposites was carried out by polymer and clay mixture method in solution. 0.5 g of the obtained polylimonene (1360 g/mol) is dissolved in 25 mL of Dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>). The solution is then stirred for 15 minutes to completely dissolve



**Figure 1.** XRD patterns of Raw-Mag, Mag-Na<sup>+</sup>, Mag-H<sup>+</sup> and Mag-CTA<sup>+</sup>.

the polylimonene. Subsequently, 2% by weight of the Mag-CTA<sup>+</sup> is added to the solution and then the mixture is treated by ultrasonic-assisted method for 3 hours. The obtained nanocomposite is precipitated in methanol, filtered and dried under vacuum over night. The same procedure is repeated for different amounts of Mag-CTA<sup>+</sup>: 3, 6, and 10% by weight to polylimonene (the synthesis of nanocomposites is described in Scheme 2). The obtained samples were named PLM-Mag (see experimental conditions in Table 2). The % yield of the obtained polymer is calculated by a simple weighing according to the following equation:

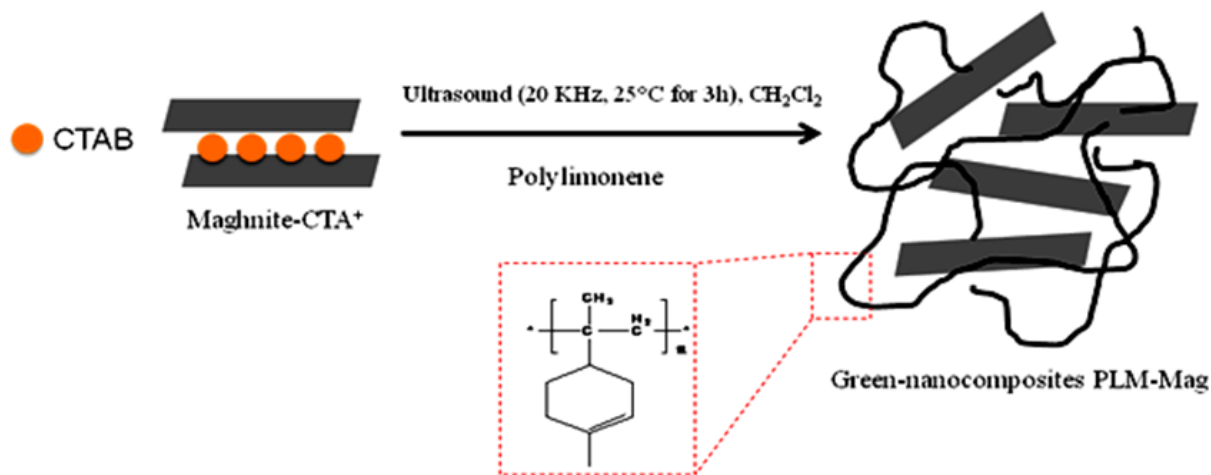
$$\text{Yield (\%)} = (M_0/M_1) \times 100\% \quad (1)$$

Where  $M_0$  is weight of the obtained nanocomposites (PLM-Mag) and  $M_1$  denotes weight of the PLM and Mag-CTA<sup>+</sup>.

### 3. Results and Discussion

#### 3.1 Characterization of Maghnite (H<sup>+</sup>, Na<sup>+</sup> and CTA<sup>+</sup>)

X-Ray diffractograms of Raw-Mag, Mag-H<sup>+</sup>, Mag-Na<sup>+</sup> and Mag-CTA<sup>+</sup> are shown in Figure 1. The calculated basal spacing ( $d_{001}$ ) from XRD



**Scheme 2.** Synthesis of nanocomposites (PLM-Mag) by ultrasonic irradiation.

**Table 2.** Experimental conditions for the preparation of nanocomposites PLM-Mag using Ultrasonification.

Samples	PLM (g)	Time (h)	Organo-clay (%)	Yield (%)	Frequency (kHz)
PLM-Mag 2%	0.5	3	2	100	20
PLM-Mag 3%	0.5	3	3	100	20
PLM-Mag 4%	0.5	3	6	100	20
PLM-Mag 10%	0.5	3	10	100	20

patterns, applying Bragg equation ( $2d \sin \theta = n \cdot \lambda$ ) is 1.01 nm for Raw-Mag and 1.52 nm for Mag-H<sup>+</sup>. This increase in basal spacing is explained by the substitution of single water between the sheet of Raw-Mag by two interlamellar water layer in Mag-H<sup>+</sup> (atomic radius of H<sub>3</sub>O<sup>+</sup> = 0.51 nm). The diffractograms of Mag-Na<sup>+</sup> and Mag-CTA<sup>+</sup> show that the interfoliar distance goes from  $d = 1.23$  nm for the Mag-Na<sup>+</sup> which corresponds to the exchange by Na<sup>+</sup> in the galleries of Maghnite (atomic radius of Na<sup>+</sup> = 0.22 nm) to  $d = 1.8$  nm for the Mag-CTA<sup>+</sup>. This increase indicates that there is intercalation of the alkyl ammonium ions of the CTAB in the inter-foliar galleries and a cationic exchange of Na<sup>+</sup> by CTA<sup>+</sup>. The addition of the alkyl ammonium ions causes a displacement of the characteristic peak of the interfoliar distance of montmorillonite towards the weak

nails (4.90 degree) for Mag-CTA<sup>+</sup>. These results show the effect of ultrasonic irradiation on the preparation of Mag-CTA<sup>+</sup>. Aicha Khenif *et al.* [25], obtained an interlayer distance of 1.98 nm during 24 h of stirring for the preparation of CTAB/Clay, in our case, an interlayer distance of 1.8 nm was obtained only in 1 h.

The IR spectra (Figure 2) of the Mag-H<sup>+</sup>, Mag-Na<sup>+</sup> and Mag-CTA<sup>+</sup> show an intense peak at 1057 cm<sup>-1</sup> and two bands at 455 and 515 cm<sup>-1</sup> relating to the elongation vibrations, and torsion of the Si-O-Si and Si-O-Al bonds respectively [26,27]. The band at 1000 cm<sup>-1</sup> due to the vibration of Si-O of the Maghnite. The bands at 1643 and 3625 cm<sup>-1</sup> are attributable to the extension of the hydroxyl groups of water bonded by hydrogen bond to clay [28]. Different bands were obtained after the modification of Maghnite by CTA<sup>+</sup>, two new bands were observed for Mag-CTA<sup>+</sup>, in the 2850 and 2922 cm<sup>-1</sup> regions corresponding to the C-H stretching vibrations of methyl group. The results obtained by FT-IR analysis show intercalation of the alkyl ammonium ions of the CTAB in the inter-foliar galleries and confirm the results obtained by XRD analysis.

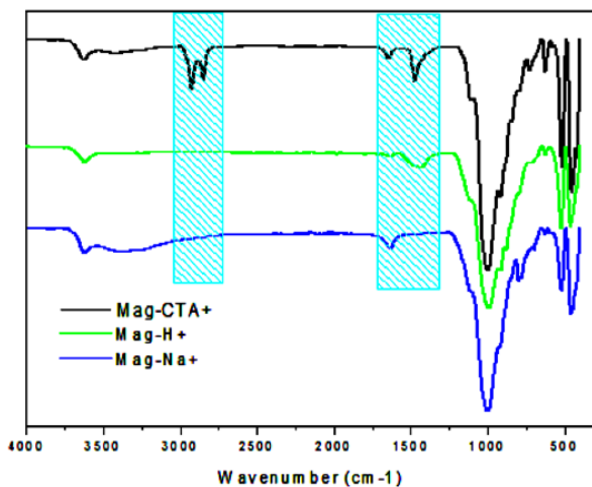


Figure 2. FT-IR spectra of Mag-CTA<sup>+</sup>, Mag-Na<sup>+</sup> and Mag-H<sup>+</sup>.

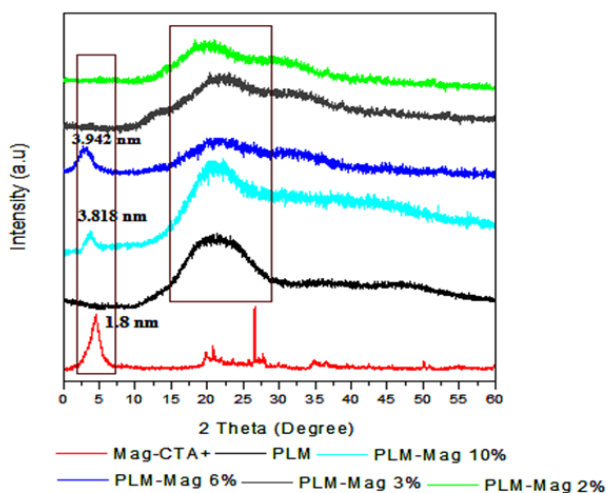


Figure 3. XRD patterns of the obtained nanocomposites PLM-Mag.

### 3.2 Characterization of Nanocomposites (PLM-Mag)

The XRD patterns of the obtained polymer and nanocomposites (PLM and PLM-Mag) are shown in Figure 3. The XRD pattern of polylimonene (PLM) presents no peak confirming its amorphous structure. This amorphous structure is observed in the nanocomposites

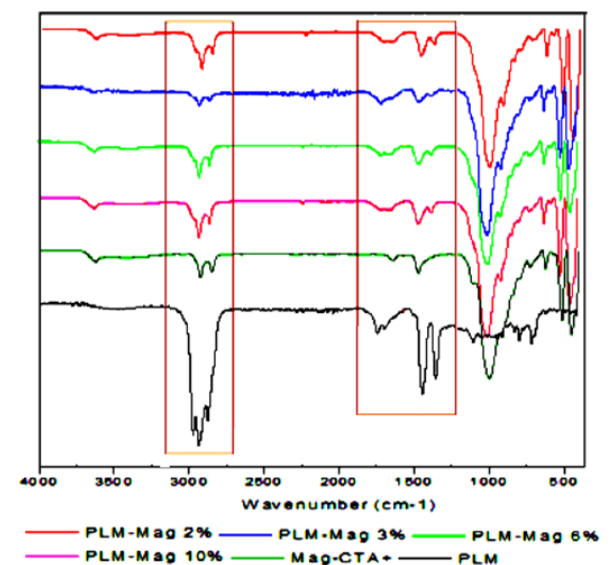
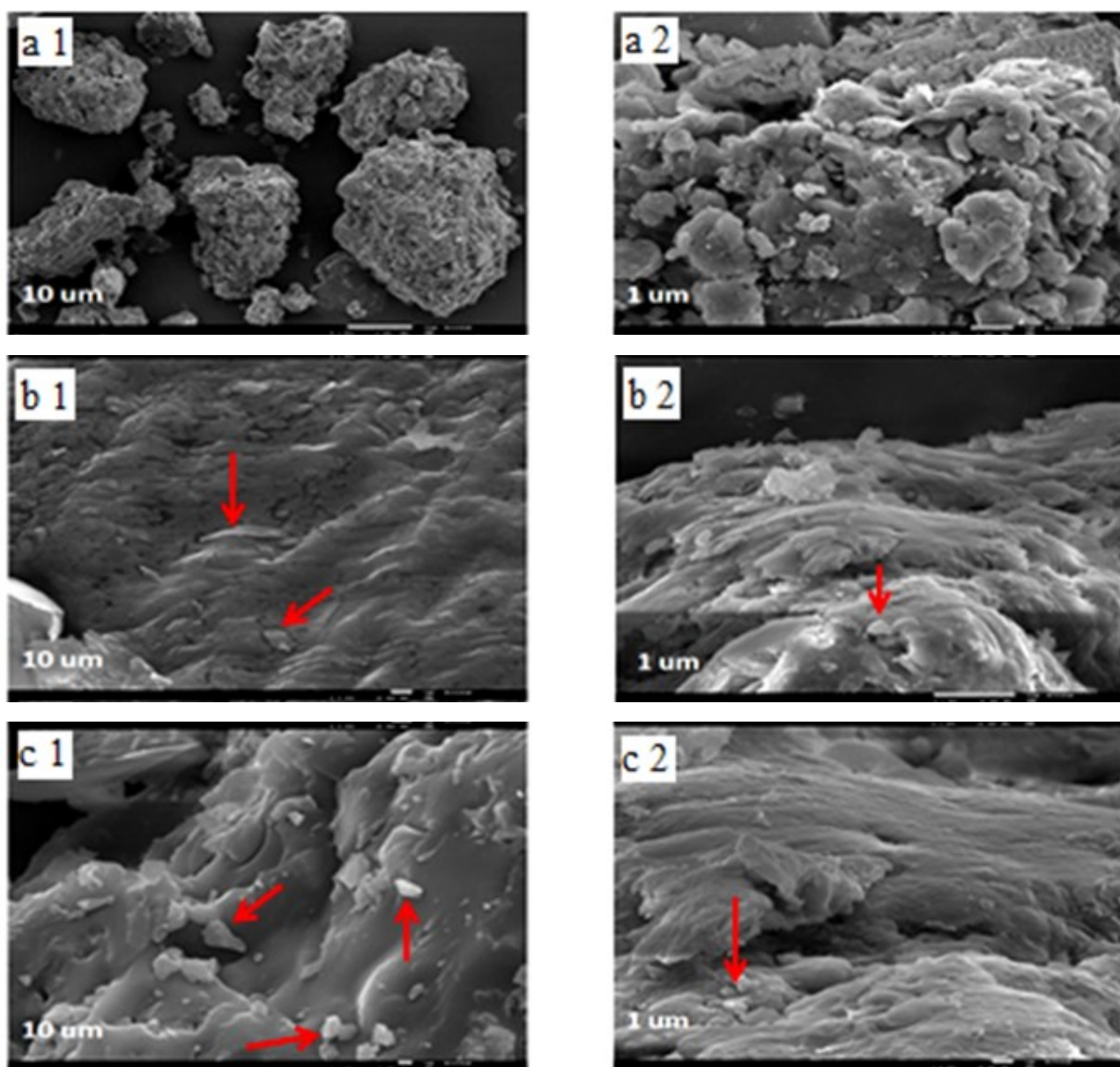


Figure 4. FT-IR spectrums of PLM and nanocomposites PLM-Mag.

with the appearance of additional peak characteristic of Mag-CTA<sup>+</sup> which confirms its good dispersion in the polymer matrix. The nanocomposites prepared by 6 and 10% by weight of Mag-CTA<sup>+</sup> showed a single peak around  $2\theta = 3^\circ$  corresponding to the interlayer distances  $d_{001} = 3.942$  and  $3.818$  nm respectively. The interlayer distance of these nanocomposites was increased more than twice compared to the Mag-CTA<sup>+</sup>, which had an interlayer distance of  $1.8$  nm. This result also confirms that the obtained polylimonene were well intercalated between the clay galleries. Except for the case of nanocomposites obtained by 2 and 3% by weight of Mag-CTA<sup>+</sup>, the diffraction peak of Mag-CTA<sup>+</sup> is not observed, confirm the exfoliation of the

clay, which explains a good diffusion of the polylimonene in the clay galleries. These results are in agreement with those obtained by Hanène Salmi-Mani *et al.* [29]. The time of the ultrasound treatment (3 h) is a key factor that can cause a formation of exfoliated nanocomposites [19]. When the cavitation bubbles reach a critical size, it can implode violently within the reaction medium, thus releasing large amounts of energy. This behavior leads to a large dispersion of the clay sheets in the PLM matrix. It can be noted that the use of ultrasound for the synthesis of nanocomposites has a great advantage compared with classic methods which take 24 h of reaction time [30].

The infrared spectra of the nanocomposites

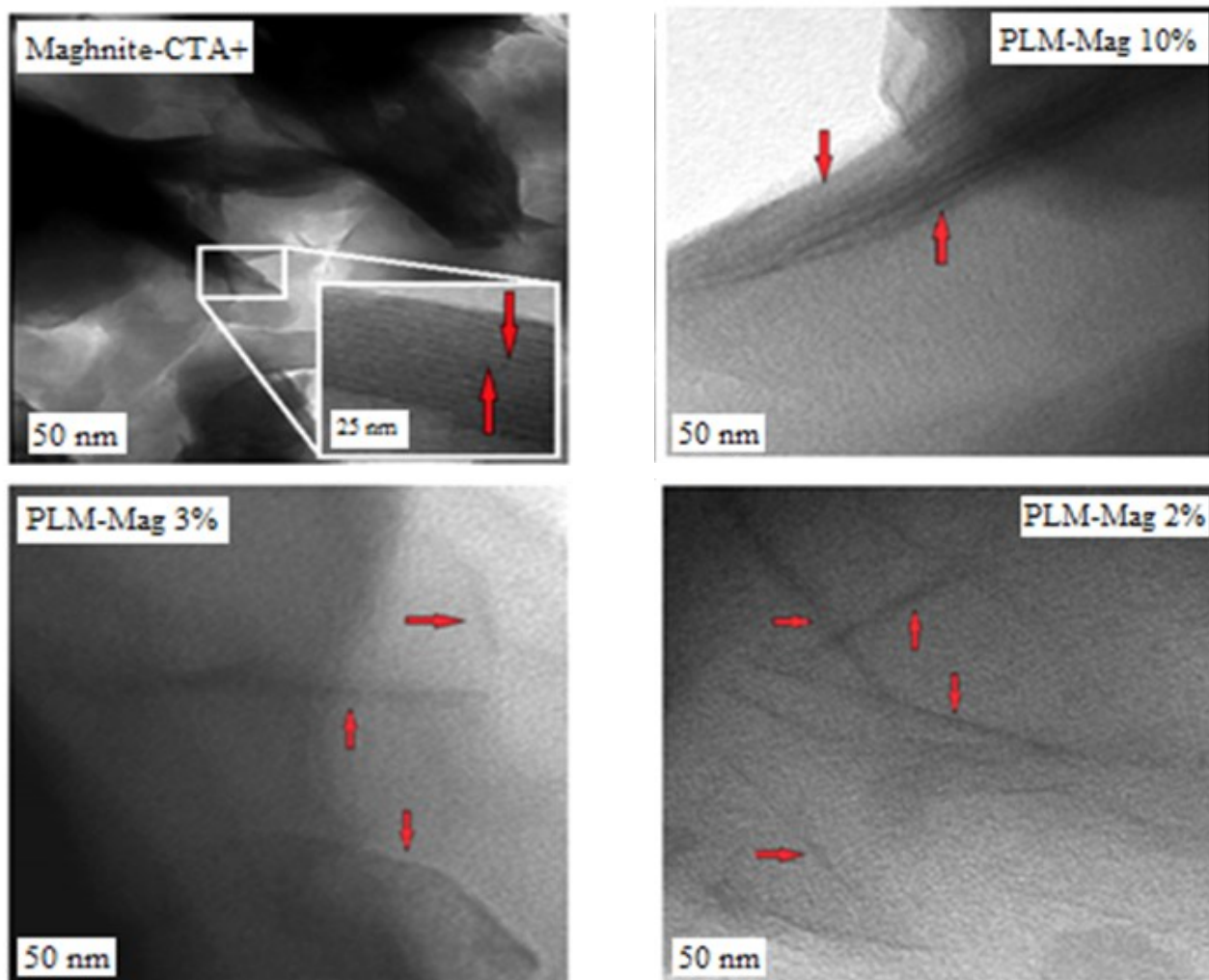


**Figure 5.** SEM images of Mag-CTA<sup>+</sup> (a1 and a2), PLM-Mag 10% (b1 and b2) and PLM-Mag 2% (c1 and c2).

(PLM-Mag 2, 3, 6 and 10%) and polylimonene (PLM) are shown in Figure 4. The infrared spectra show that the polylimonene and the nanocomposites have almost the same vibration bands overlapping with the vibration bands of the organo-modified clay (Mag-CTA<sup>+</sup>) and the FT-IR spectra show that the obtained nanocomposites PLM-Mag are in a good agreement with the polylimonene structure. The adsorption band at 1673 cm<sup>-1</sup> corresponds to the double bond C=C in the polylimonene was observed in the FT-IR spectra of the obtained nanocomposites. The C-H symmetry and asymmetry stretching of the methyl and methylene group was observed at 2922 and 2935 cm<sup>-1</sup>. These results confirm the interaction of the functional group of PLM with the internal surface of clay. Compare to the FT-IR spectrum of the pure PLM, the spectra of the obtained nanocomposites show the appearance of the intense peak at 1000 cm<sup>-1</sup> corresponding to the

vibration of Si-O of the Mag-CTA<sup>+</sup>. However, the absorption bands observed on the FT-IR spectra of pure PLM and Mag-CTA<sup>+</sup> are gathered on the FT-IR spectra of the obtained nanocomposites. These results show the intercalation of polylimonene in the interlayer montmorillonite gallery.

Figure 5 shows the SEM images of the organo-modified clay (Mag-CTA<sup>+</sup>), the intercalated nanocomposites (PLM-Mag 10%) and the exfoliated nanocomposites (PLM-Mag 2%). The comparison of the Mag-CTA<sup>+</sup> morphology (Figure 5 a1 and a2) with the first nanocomposites PLM-Mag 10% (Figure 5 b1 and b2) shows a more organized small particle structure of montmorillonite. In the nanocomposites PLM-Mag 2% (Figure 5 c1), the observation of nanocomposites at 10 μm reveals a formation of montmorillonite plate separated, that is a partial exfoliation, the same sample observed at 1 μm (Figure 5 c2), shows a rougher surface

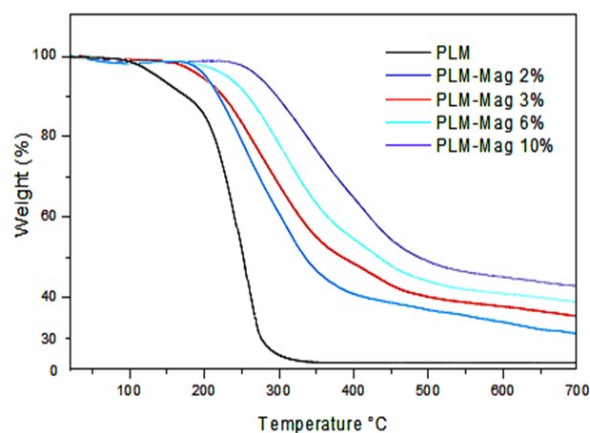


**Figure 6.** TEM images of Mag-CTA<sup>+</sup>, PLM-Mag 10% (intercalated), PLM-Mag 3% (exfoliated) and PLM-Mag 2% (exfoliated).

and a covering of the montmorillonite surface by the polylimonene.

The transmission electron microscopy was used to determine the dispersion of Mag-CTA<sup>+</sup> in polylimonene matrix and also to compare the results obtained by the XRD analysis. The TEM images of Mag-CTA<sup>+</sup> and the obtained nanocomposites PLM-Mag (2, 3, and 10%) are shown in Figure 6. For Mag-CTA<sup>+</sup>, it is easy to define the silicate layers by the dark and bright lines. The nanocomposite (PLM-Mag 10%) prepared by 10% of Maghnite-CTA<sup>+</sup> shows an intercalated structure of the modified clay. However, the nanocomposites (PLM-Mag 2 and 3%) show a partial or total exfoliated structure and the clay nanoparticles are mainly well dispersed in the polylimonene matrix. These results confirm the results obtained by XRD analysis. This also explains the beneficial effect of ultrasound on the dispersion of clay in the PLM matrix. The effect of ultrasound also gives better yields compared to the in-situ polymerization synthesis method [30].

Thermogravimetric analysis was carried out under nitrogen with a heating rate of 20 °C/min. Figure 7 shows the TGA curves of pure polylimonene and that of nanocomposites of 2, 3, 6, and 10% by weight of Mag-CTA<sup>+</sup>. It can be seen that the pure polylimonene and all its nanocomposites exhibit a one-step weight loss mechanism. The nanocomposites show a high thermal stability up to a degradation temperature of 200–250 °C, while the degradation temperature of pure polylimonene observed about 140 °C. In addition, the intercalated nanocomposites (PLM-Mag 10%) prepared with 10% of Mag-CTA<sup>+</sup> showed highest thermal stability with a degradation temperature of 250 °C. These results show that the thermal stability of



**Figure 7.** TGA curves of PLM and PLM-Mag (2, 3, 6, and 10%).

the obtained nanocomposites is not only related to the clay content, but it is also much more related to the state of the clay in the polymeric matrix, it is related to the surface area between the polymeric matrix and the clay. This gain in thermal stability is due, according to previous work [31], to the formation of a protective carbonized layer. The formation of this layer is favored by the fine dispersion of intercalated or exfoliated particles of montmorillonite which play an inorganic support role [32]. In general, the degradation temperature of the polymers is increased after the incorporation of exfoliated lamellar silicates [33–35], which values these polymers and allows their use at higher temperatures.

#### 4. Conclusion

The effect of organo-modified clay (Mag-CTA<sup>+</sup>), prepared and used with different ratios, on the nanocomposites polylimonene/Maghnite properties is studied. The XRD results indicate that the nanocomposites prepared with 2 and 3 %wt of Mag-CTA<sup>+</sup> were exfoliated, and the nanocomposites prepared with 6 and 10 %wt of Mag-CTA<sup>+</sup> were intercalated, leading to an expansion of the interlayer distance between the layers. Thermogravimetric results indicate that the nanocomposites present a high thermal stability compare to the pure polylimonene ( $T < 250$  °C). This is attributed to the interactions between all the polymer chains and the organic compounds of the modified clay. The reinforcing effect of the clay in the polymer is confirmed by increasing the rigidity of the system. The morphology study by SEM and TEM of the obtained nanocomposites confirmed an organization of certain particles, and in other cases a separation in plates made up of montmorillonite layers. This confirms partial or total exfoliation of montmorillonite in the polymer matrix and formation of the nanocomposites. In general, the data show that CTAB is effective for the preparation of organophylic clay.

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