

Preparation and Characterization of Clay (Maghnite-H)/Poly(3,4-Ethylenedioxythiophene) Composites

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ABSTRACT

Composites of Maghnite-H, a Montmorillonite sheet silicate clay, exchanged with protons, and Poly(3,4-ethylenedioxythiophene) (PEDOT) were prepared by *in situ* chemical polymerization of the 3,4-ethylenedioxythiophene, without the use of solvent or oxidant. The effect of changing monomer/clay ratio was studied and the resultant composite structures were characterized by Inferred spectroscopy, ²⁷Al and ¹³C Solid-State NMR spectroscopy, scanning electron microscopy and powder X-ray diffraction. All analyses are consistent with a structure where the polymer is (partially) intercalated into the clay structure, which in favourable cases lead to exfoliation. The presence of the clay in the polymer leads to a desired increase in thermal stability as witnessed by thermogravimetry.

Keywords: Poly(3,4-Ethylenedioxythiophene); PEDOT; Clay; Maghnite-H; Montmorillonite

1. Introduction

Polythiophene and its derivatives have attracted much interest over recent decades due to exceptional electrical properties and their environmental stability [1-6]. From this class of conducting polymers with conjugated π -bonds, especially poly 3,4-ethylenedioxythiophene (PEDOT) possess unique properties such as high environmental stability [7,8] and a small band gap (1.6 - 1.7 eV); a direct consequence of the electron donation properties of the ether functionality [9]. In addition, the electronic conductivity can reach as high as 300 S/cm after the polymer has been oxidized [10]. These characteristics have lead to several applications, such as antistatic paints [11,12], electrochromic devices [13,14], electrochemical capacitors [15], biosensors [16-18], polymer solar cells (PSCs) [19,20], polymer light-emitting diodes (PLEDs) [21,22] etc. Polymerisation of EDOT may be accomplished by either electrochemical or chemical oxidation. Both techniques lead to a material which in his native state is insoluble and cannot be melted below the decomposition temperature [6,23]. This problem has been resolved by researchers at Bayer AG., Germany, by persulfate oxidative polymerization in a solution containing a polyelectrolyte (polystyrene sulfonic acid) [24]. More recently, aqueous solvated nanoparticles of PEDOT have been prepared using ammonium perdisulfate and

the surfactant dodecylbenzene [25]. Another approach to polymer structures with nanometer dimensions is to form clay/polymer hybrids. These hybrids have found numerous applications due to their mechanical properties, their thermal stability and their reduced permeability to gases [26]. Recent examples include hybrids of clay and polyaniline [27,28], and clay and polypyrrole [29]. An especially elegant approach to these composites is the solvent-free direct reaction between the clay and the monomer, where the clay serves the double role of reactant/catalyst for the polymerization and inorganic component of the final hybrid material. In this manner Biswas *et al.* [30,31] have prepared composites of Poly(N-vinylcarbazole) and polypyrrole by direct reaction with montmorillonite. Sadok *et al.* [32] have prepared polypyrrole composites by using a clay montmorillonite naturally rich in ions or synthetically doped with ions (Saponite substituted with Fe³⁺ in tetrahedral sites). Surprising little clay composite studies have been performed on polymers which contain the thiophene functionality. A notable exception is Ballav *et al.* [33] who have succeeded in preparing composites polythiophene/montmorillonite, by solvent-free direct reaction between the monomer and montmorillonite-Na⁺. The composites produced showed that the polythiophene was intercalated in the interlayer space and that the resultant material showed a modest but non-zero electronic conductivity on the order of 10⁻⁴

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S/cm.

In this article, we examine the use of Maghnite-H⁺ (MagH), a Montmorillonite sheet silicate, in the synthesis of composites with PEDOT. The choice of MagH is based on related work where it acts as a catalyst of cationic polymerization of vinyl [34-37] and heterocyclic [38-42] monomers. Here the synthesis takes place in a one pot reaction between the clay and the monomer without the use of solvent or oxidant. Specifically, we examine the effect of the relative ratios between the monomer and the clay on the intercalation and possible exfoliation of the clay structure.

2. Experimental

2.1. Materials

MagH was prepared using the method of Belbachir *et al.* [34]. EDOT was obtained from Bayer AG. (Leverkusen, Germany) and used without further purification.

2.2. Synthesis

All reactions were performed using the same methodology described below, with however, a variation of time, for the 10% by weight of MagH/monomer 24 h reaction and for 50% 96 h reaction. The reaction times and relative concentration were altered according to **Table 1**.

Hybrides from 10% by weight of MagH/monomer reaction mixtures.

In a round bottom flask fitted with a condenser was mixed 1 g (0.007 mol) EDOT and 0.5 g MagH previously dried at 100°C overnight. The mixture was heated to 90°C, under constant stirring using a magnetic stir bar. Upon the addition of the MagH a colour change was witnessed from clear over red to brown before finally becoming dark green. After 24 h of heating a black solid was formed, and the suspension was cooled to room temperature. Residual unreacted monomer and shorter solvable oligomers were removed by washing with dichloromethane. The residual black solid (the hybrid material) was dried at 60°C overnight to remove any solvent traces. (Calculate a real yield based on incorporated polymer relative to the initial amount). The amount of incorporated polymer was determined to 21 m/m-% based on the mass gain.

2.3. Characterization

Infrared spectra (400 - 4000 cm⁻¹) were collected from samples ground with dry KBr and pressed into pellets. Spectral peaks around 2350 cm⁻¹ stem from residual CO₂ in the beam path. ¹³C and ²⁷Al Solid state NMR was performed using a BRUKER ASX 400 CP-MAS. Thermogravimetric analysis (TGA) was performed on a Standon Redcroft STA780 thermal analyser and in air at a heating rate of 5 deg/min within the temperature range of 25°C - 1000°C. The powder X-ray diffraction (XRD) patterns of the samples were recorded using Philips XRD X'PERT PRO II diffractometer (2 goniometers, Montpellier, French) using Cu-K α radiation and ($\lambda = 1.5404 \text{ \AA}$) produced at 40 kV and 40 mA. Scanning electron microscopy micrographs were collected on a Hitachi S-2600N with a 25 kV working potential, a working distance of 7.0 - 7.4 mm and a SE detector.

3. Results and Discussion

3.1. Characterization by Infrared Spectra (IR)

Figure 1 shows, respectively, the spectra IR of MagH, the composites MagH-PEDOT (1): B and MagH-PEDOT (2): C and of polymer PEDOT: D Vibrations around 1337 and 1518 cm⁻¹. (B, C, D) are due respectively to the elongation of C-C and C=C bonds of the thiophene cycle, these peaks do not appear in the IR spectrum of MagH. Peaks located at 980, 833 and 794 cm⁻¹ are due to the vibrations of the CS bond in thiophene, and signals around 1080 cm⁻¹ indicate C-O-C bond of the ethylenedioxy group. The weak peaks from 2854 to 2925 cm⁻¹ show the CH elongations of ethylene related to the thiophene cycle. All IR peaks found in the composites, compared with the peaks of MagH and PEDOT, confirm the presence of PEDOT in the composites. Kvarnstrom and *et al.* [9] and Jeong *et al.* [25] have obtained same results in the synthesis of the PEDOT.

3.2. Characterization by ¹³C Solid State NMR

The solid ¹³C NMR spectrum of the composite MagH-PEDOT (1) shown in **Figure 2**, shows three peaks characteristic of PEDOT, a peak at 110 ppm of C1 carbon related to the sulphur atom, a second at 140 ppm of sp² carbon (C₂), and a third at 65.87 ppm of the sp³ carbon (C₃) of the cyclic ethylene related to thiophene. The

Table 1. Operating conditions of the synthesis of the MagH-PEDOT hybrids.

Hybride MagH-PEDOT	EDOT (g)	MagH (%)	Temperature (°C)	Time (h)	Yield of the grafted PEDOT (%)
(1)	0.5	50	90	24	21
(2)	0.6	10	90	96	80

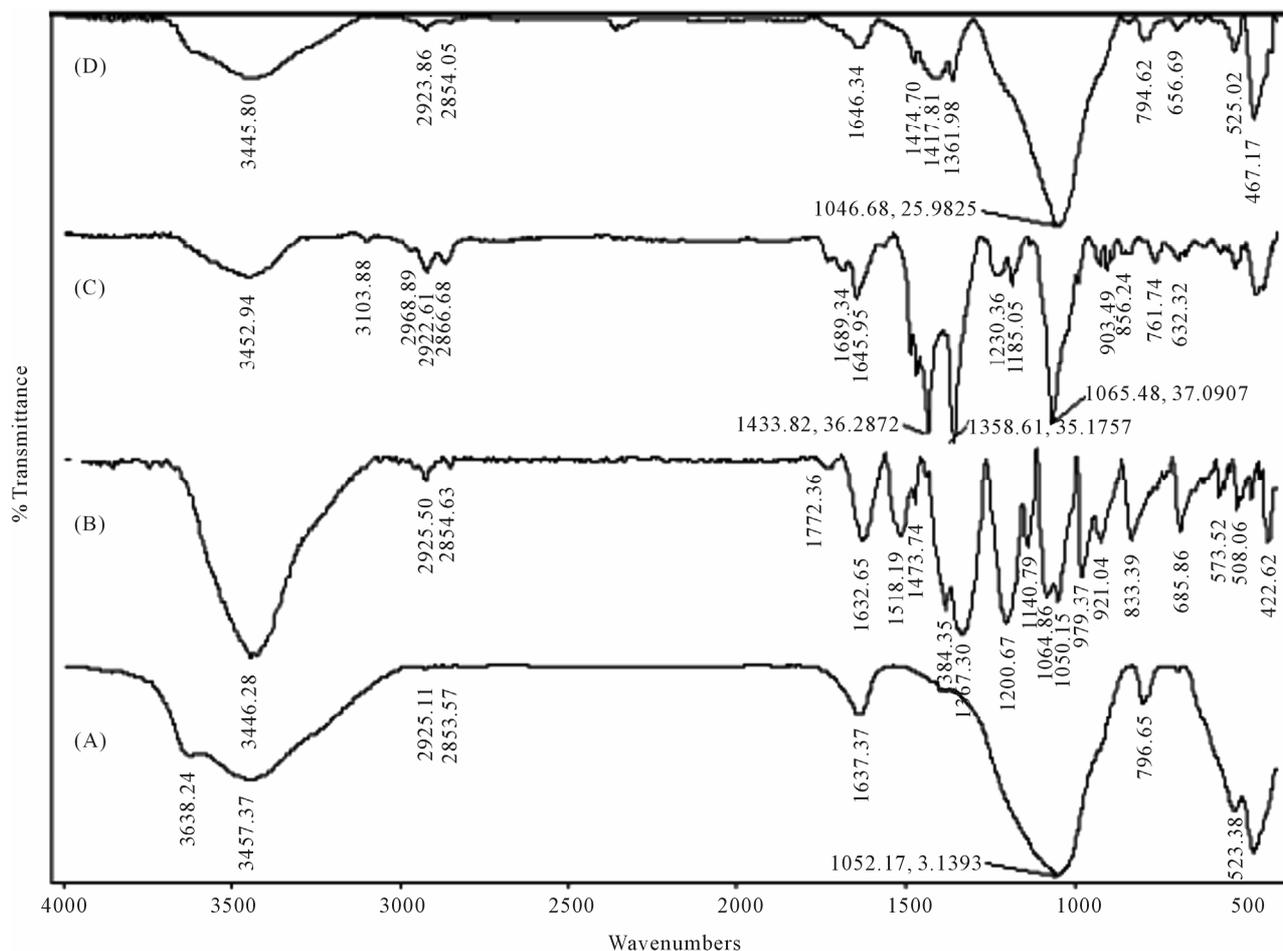


Figure 1. IR spectrums of (A) Maghnite-H⁺ (MagH); (B) PEDOT, prepared with FeCl₃; (C) Hybrid MagH-PEDOT (10% MagH, 96 h, 90°C); (D) Hybrid MagH-PEDOT (1) (50% MagH, 24 h, 90°C).

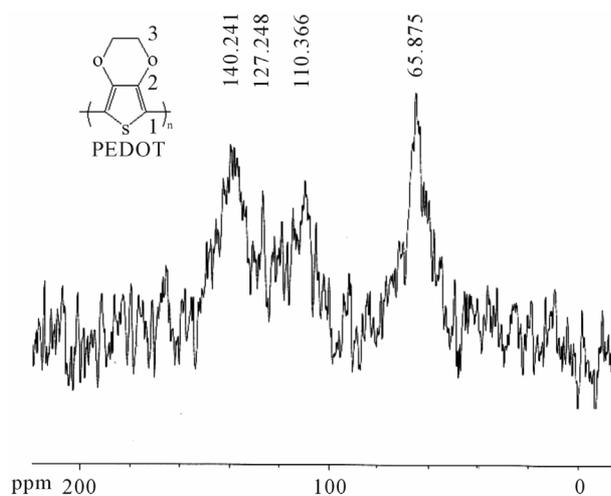


Figure 2. ¹³C solid state NMR spectrum of hybrid MagH-PEDOT (1), obtained with 50% MagH, 24 h, 90°C.

structure obtained is similar to that found by Meng *et al.* [43], which confirms the presence of PEDOT in the MagH-PEDOT composite.

3.3. Characterization by X-Ray Diffraction (XRD)

The reticular distances d_{001} of interfoliaceous space, were calculated from X-ray diffractograms of the hybrids and Montmorillonite (MagH), by using K_{α} radiation of the copper anode with λ (Cu) = 1.5404 Å, and in the MagH-PEDOT (b) hybrid. The characteristic montmorillonite peak reaches 13.26 Å for $2\theta = 6.65$ (**Figure 3(A)**), the montmorillonite peak in MagH appears to an interfoliaceous distance of 12.87 Å (**Figure 3(A)**). The **Figure 3(B)** shows the displacement of the montmorillonite peak in the composite MagH-PEDOT (b) towards the weak angles, compared with that of MagH. Thus, in the case of the MagH-PEDOT (b) composite, the intercalation of PEDOT between the layers of montmorillonite (MagH) has taken place. The same results were observed in the case of the composites of PNVC-MMT with an interfoliaceous space $d_{001} = 14.6$ per $2\theta = 6.9$, which indicates the intercalation of polymer PNVC in montmorillonite MMT [24]. On the other hand, the diffractogram of the MagH-PEDOT (c) hybrid (**Figure 3(A)**), presents an ab-

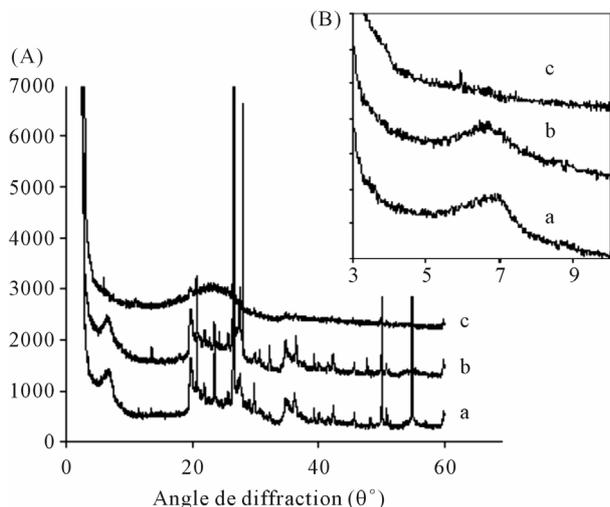


Figure 3. (A) XRD patterns of MagH (a) and hybrids MagH-PEDOT (b, c) obtained with, (b) 50% MagH, 24 h, 90°C and (c) 10% MagH, 96 h, 90°C; (B) XRD enlargement in area of the diffraction angle (θ): 3 - 10.

sence of the characteristic peak of montmorillonite, and also of the amorphous zones, which results in a broad peak, and an partially exfoliation of montmorillonite in the MagH-PEDOT (c) composite.

3.4. Determination of the Composites Morphology

The comparison of the MagH SEM morphology (**Figure 4(A)**) with the first hybrid MagH-PEDOT (**Figure 4(B)**) shows a montmorillonite structure more organized in small particles. In the sample MagH-PEDOT hybrid (**Figures 4(C)** and **(D)**), the observation of the hybrid at 20 μm (**Figure 4(C)**), reveals a formation of montmorillonite plate separated, that is a partial exfoliation, this result is in the same way than results obtained by DRX analysis, the same sample observed at 10 μm (**Figure 4(D)**), shows a rougher surface and a covering of the montmorillonite surface by the PEDOT.

3.5. Characterization by ^{27}Al Solid State NMR

The ^{27}Al NMR data (**Figure 5**) show that the octahedral and tetrahedral Aluminium peaks are preserved in the MagH-PEDOT (1) composite, compared to the octahedral and tetrahedral peaks of MagH (**Figure 6**), thus PEDOT does not form a bond with aluminium, or is not in the aluminium environment.

3.6. Thermal Stability of Composites (Thermogravimetric Analysis: TGA)

The thermograms of **Figure 7** show that MagH brings a greater stability to the composites, more the product is rich in polymer more it is degraded easily. Thus, the sta-

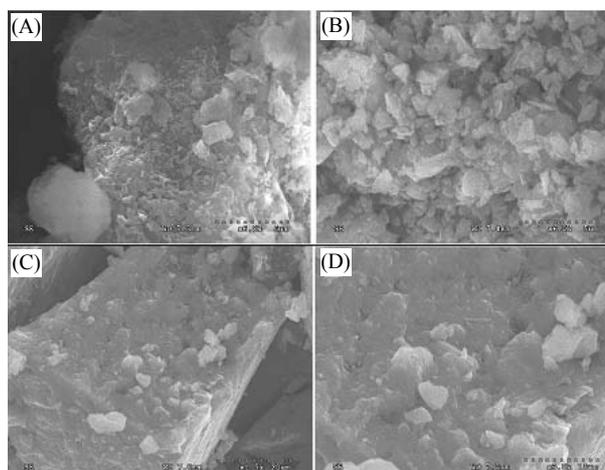


Figure 4. The scanning electron micrographs images of MagH (A) hybrids MagH-PEDOT (B) obtained with 50% MagH, 24 h, 90°C; and MagH-PEDOT (C), (D) obtained with 10% MagH, 96 h, 90°C, with a work distance: 7.0 - 7.4 mm and an amplification: 1.5 - 6.0 k.

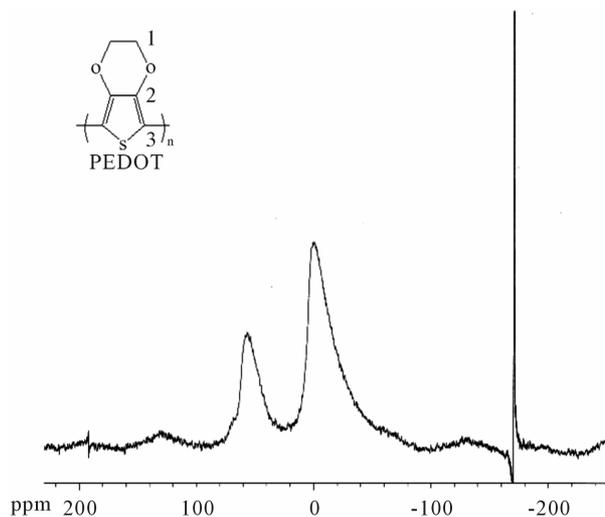
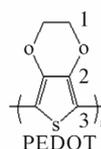


Figure 5. Spectrum ^{27}Al solid state NMR of hybrid MagH-PEDOT (1): obtained with 50% MagH, 24 h, 90°C.

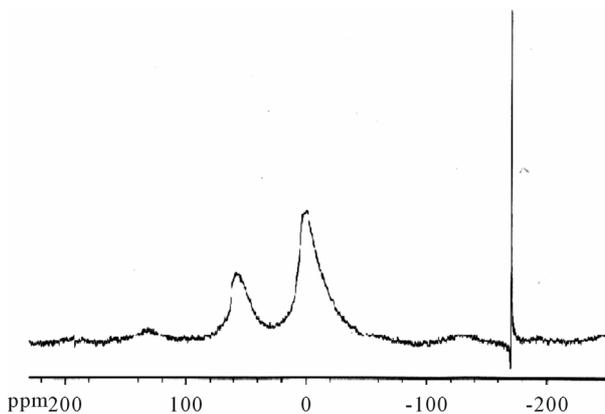


Figure 6. Spectrum ^{27}Al solid state NMR of MagH.

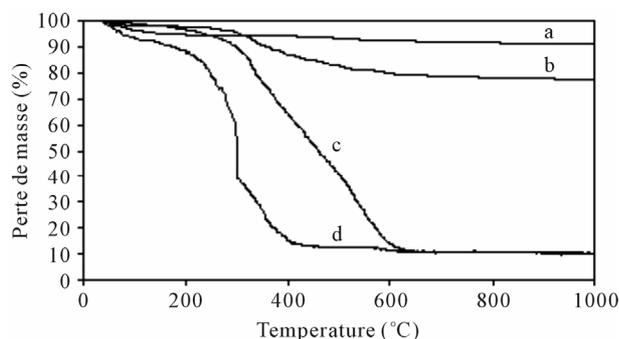


Figure 7. TGA curves of: (a) (MagH); (b, c) MagH-PEDOT; (b) obtained with 50% MagH, 24 h, 90°C; (c) obtained with 10% MagH, 96 h, 90°C; (d) PEDOT.

bility order obtained for all materials is as follows: MagH-PEDOT (b) > MagH-PEDOT (c) > PEDOT. Similar results were observed for the montmorillonite/polythiophene composites (MMT-PTP) [27]. The percentage of the PEDOT grafted, determined from thermograms, is 19% in the MagH-PEDOT composite (**Figure 7(b)**) whereas it is 89% in the MagH-PEDOT composite (**Figure 7(c)**).

4. Conclusion

The *in situ* polymerization of 3,4-ethylenedioxythiophene (EDOT) by MagH, led to the synthesis of the MagH-PEDOT hybrids. The DRX study of MagH-PEDOT hybrids shows an intercalation of PEDOT between the MagH layers and a partial exfoliation in certain hybrids rich in PEDOT. The morphology study by SEM of hybrids confirmed an organization of certain particles, and in other cases a separation in plates made up of montmorillonite layers. This confirms partial exfoliation of montmorillonite in the hybrids and formation of the composite. The ^{27}Al solid state NMR shows that the polymer is not in the environment of aluminium. The thermal analysis of hybrids and montmorillonite shows a high thermal stability of composites and that it is possible to quantify intercalated polymer.

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