



Synthesis and characterization of poly(3,4-ethylenedioxythiophene)/ Montmorillonite nanocomposites using surfactants modified clay

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Nanocomposites of Poly (3,4-ethylenedioxythiophene) (PEDOT) and surfactant modified Maghnite clay have been successfully synthesized by in situ polymerization of EDOT monomer in the interlayer space of the organoclay. The synthesis has been assisted by ultrasonic method to improve the dispersion of PEDOT polymer between the Maghnite clay sheets. The surfactant modified clay is synthesized via cation exchange method with Hydrogenure Tetrabutylammonium (TBAHS) and cetyltrimethylammonium (CTAB). Two types of organo-modified clays are obtained namely the Mag-TBA and Mag-CTA according to the template used. Various physico-chemical techniques are used for nanocomposites characterization such as XRD, FTIR, AFM, TGA/DTA, SEM and TEM. The results prove the formation of intercalated / exfoliated upon increasing the content of organoclay in the nanocomposites, consequently, different morphologies and structures in which the exfoliated and intercalated forms were obtained. Both nanocomposites display significant enhancement in the thermal stabilities compared to the PEDOT polymer. However, a decrease in conductivity values is observed for all samples compared to pure conducting polymer. This feature can be improved in view of desired application in electrochemical devices.

Keywords: Characterization, Montmorillonite, Nanocomposites, Organoclay, Poly(3,4Ethylenedioxythiophene), Surfactants

The polymer materials have attracted much attention due to their interesting properties different from those of conventional materials. At present, the central challenge is how to improve the high-performance characteristics of polymer-based matrices. In this context, the polymeric materials used for the fabrication of advanced components should exhibit the desired physicochemical properties such as mechanical strength and stiffness, thermal stability, and chemical resistance¹⁻⁴. The nanocomposites materials are most widely studied by the researches laboratories owing to their improved properties. Among the materials used in this field is the montmorillonite (MMT) clay. MMT is composed of silicate layers with 1 nm in thickness and 0.2–2.0 μm in the lateral dimensions. Its layers consist of an octahedral sheet sandwiched between two tetrahedral sheets. In natural clay the negatively charged layers are balanced by exchangeable small inorganic cations. This cation can be also exchanged by organic compounds into the interlayer spaces. Organomodified clays are commercially available or can be prepared using a range

of cationic surfactants such as cetyltrimethylammonium bromide (CTAB) and Sulfate of Hydrogenure Tetrabutylammonium (TBAHS). The modified clay can be used as host materials for in situ polymerization due to their extended interlayer space⁵. Polymers with high conductivity, including poly(3,4-ethylenedioxythiophene) (PEDOT), have attracted particular interest due to their excellent chemical and thermal stability, low redox potential^{6,7}, regular structure, low bandgap, and good electrochromic behaviour^{8,9}. Owing to these interesting properties, The PEDOT polymer is currently one of the conductive polymers used, with applications in energy conversion and sensing devices as well as in bioelectronics.¹⁰ The EDOT monomer can be polymerized by electrochemical or chemical oxidation. Both processes produce a pure insoluble material that is unable to melt below the decomposition temperature^{11,12}. Recently, nanoparticles of PEDOT in an aqueous medium have been developed from ammonium persulphate and the surfactant dodecylbenzene¹³. Ballav *et al.* made an exception

by preparing polythiophene/montmorillonite nanocomposites by directly reacting to the monomer and montmorillonite- Na^+ without solvent¹⁴. Nanosized polymer structures are also likely to form clay/polymer hybrids. Such hybrids have many applications due to their mechanical properties, thermal stability, and reduced gas permeability¹⁵. As far as we have able to ascertain, the combination between surfactants modified Maghnite clay and PEDOT polymer has not been studied. This study aimed to obtain and characterize nanocomposites from Algerian clay called "Maghnite" and PEDOT conductive polymer. We first deal with the modification of Maghnite, using different concentrations of cetyltrimethylammonium bromide (CTAB) and Sulfate of Hydrogenure Tetrabutylammonium (TBAHS). The clays thus obtained were then used as host and green nano-reinforcements for the preparation of PEDOT /Orgnaophilic clay nanocomposites. For this study, we have studied the effect of different loading rates of nanoclays (NC) modified with two types of surfactants to evaluate the physicochemical and thermal characteristics of the developed material. A detailed study of the structural, thermal and morphological properties was carried out to obtain a good overview of the main parameters that can be controlled to determine the structure of the nanocomposite.

Experimental Section

3,4 Ethylenedioxythiophene (EDOT) monomer ($\geq 99\%$ purity) and potassium peroxydisulphate ($\text{K}_2\text{S}_2\text{O}_8$, $> 80\%$), cetyltrimethylammonium bromide (CTAB), sulfate of hydrogenure tetrabutylammonium (TBAHS). All these reagents were used as received from Sigma-Aldrich. The montmorillonite clay used in this study was supplied by ENOF Maghnia society situated in the west of Algeria and used as received.

Preparation process for maghnite- organophilic

The organomodified clays were elaborated according to the cation exchange method. In a typical synthesis, 10g of Maghnite- Na^+ were dispersed into one liter of

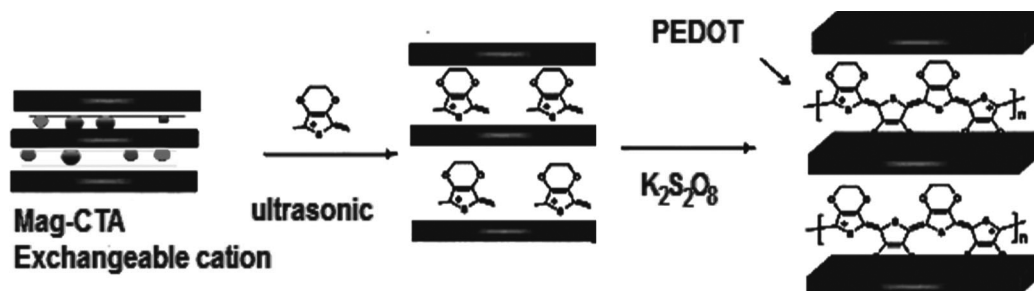
distilled water containing two determined concentrations of surfactant (CTAB, TBAHS). The organophilic activation was performed by ultrasonic method. The obtained product was filtered and washed several times with distilled water. The final product was vacuum dried oven at 120°C ¹⁶⁻¹⁸. The obtained nanocomposites were labelled as Mag-TBA and Mag-CTA.

Preparation of PEDOT /Maghnite nanocomposites

Different poly(3,4 ethylenedioxythiophene)-clay nanocomposites have been prepared using different amounts of modified clays corresponding to 1,3, 5,7 and 10% by weight based on the initial amount of 3,4 ethylenedioxythiophene. PEDOT/Maghnite nanocomposites were elaborated by intercalation and in situ polymerization reaction of EDOT monomer using the modified Maghnite. The Maghnite clay used in this study plays a role of both initiator and reinforcement of the nanocomposite. In a typical synthetic way: 1 g of EDOT monomer was added to various percentages of organophilic clay (1, 3, 5, 7, and 10 %). For a good dispersion, the mixtures were stirred at room temperature for 30 min using an ultrasonic generator at 400 rpm. Then, the $\text{K}_2\text{S}_2\text{O}_8$, used as oxidant (0.05M), was introduced into the reaction mixture according to the different concentrations of surfactants modified clay. The polymerization reaction was then carried out at 70°C for 6 h. Each sample obtained at the end of the reaction was then filtered, washed with distilled water, and dried at 70°C under reduced pressure. The final products in a form of black powder were labelled as PEDOT /Mag-TBA and PEDOT/Mag-CTA (Scheme 1)¹⁹. The preparation conditions for both nanocomposites PEDOT /Mag-TBA and PEDOT/Mag-CTA are collected in Table 1.

Characterization

The Infrared absorbance spectra were recorded using an ATIMATTSON type FTIR Spectrometer in the spectral range $400 - 4000 \text{ cm}^{-1}$. The X-ray diffraction measurements were carried out with a powder



Scheme 1 – Schematic way in the synthesis of PEDOT/Maghnite-CTA nanocomposite.

diffractometer (Philips, model PW 1830) by using $K\alpha_1$ copper radiation ($\lambda=1.54\text{\AA}$). The SEM images have been taken using a scanning electron microscope (model type Jeol 5610, Japan). The TEM analysis have been processed by ultra-microtomy under cryostatic conditions, producing sections approximately 20 nm thick. These sections were analyzed with the HRTEM Jeol-2011(Japan) electron microscope under an acceleration voltage of 200 kV. The thermo-gravimetric analysis (TGA) and differential thermal analysis were performed using Setaram LabsysTM DTA, DSC, TGA, TMA instruments between 20 and 1600°C (nominal 1400°C) with a heating rate of 10°C/min., it was carried out for pure PEDOT and their nanocomposites. The four-point method was used for electrical measurements using an ohmmeter (Advantest, Digital Electrometer, TR8652). The electrical resistances of the pellets were evaluated using a two-point probe technique using a digital multimeter (Fluke 8845A) in dry air. The atomic

force microscopy (AFM) topographic images were made using a PicoSPM molecular imaging system equipped with a NanoScope IV controller under ambient conditions. The mean effective roughness (R) was determined using the statistical application of the Nanoscope software, whose nanometric measurements were obtained under ambient conditions at 50% humidity and 20-25°C. The system was installed on a vibration isolation active table with minimal acoustic disturbance.

Results and Discussion

FT-IR analyses

The FT-IR spectra of PEDOT, organic clay, and PEDOT /Mag-CTA nanocomposite are shown in Fig. 1. As can be seen from the Fig. 1(A), the infrared spectra of PEDOT shows vibrations around 1309 and 1524 cm^{-1} which are assigned to the thiophene ring. The two vibration frequencies are attributed to C-C and C=C stretching of the quinoidal structure of the thiophene ring. The absence of peaks at 1490 and 1190 cm^{-1} indicates that the monomer form has transformed to polymeric form.²⁰ In Figs 1(B) and 1(C), the peak at 3629.4 cm^{-1} is assigned to the OH group linked to the aluminium in octahedral coordination. In addition, the two bands at 1012 and 481 cm^{-1} are due to the deformation vibrations of Si-O-Si. In Fig. 1(C), the IR spectra of the surfactants modified Maghnite, revealed the presence of new bands at 3011, 2931, 286, 1490 and 1446 cm^{-1} , assigned to N-(CH₃)⁺, asymmetric CH₂, symmetric

| Organo-clays (%) | Pedot (g) | Time (h) | Yields (%) |
|------------------|-----------|----------|------------|
| PEDOT/Mag-TBA | 1 | 24 | 96.6 |
| PEDOT /Mag-TBA | 1 | 24 | 82.4 |
| PEDOT /Mag-TBA | 1 | 24 | 71.2 |
| PEDOT /Mag-TBA | 1 | 24 | 69.1 |
| PEDOT /Mag-CTA | 1 | 24 | 78.9 |
| PEDOT /Mag-CTA | 1 | 24 | 69.7 |
| PEDOT /Mag-CTA | 1 | 24 | 61.4 |
| PEDOT /Mag-CTA | 1 | 24 | 58.3 |

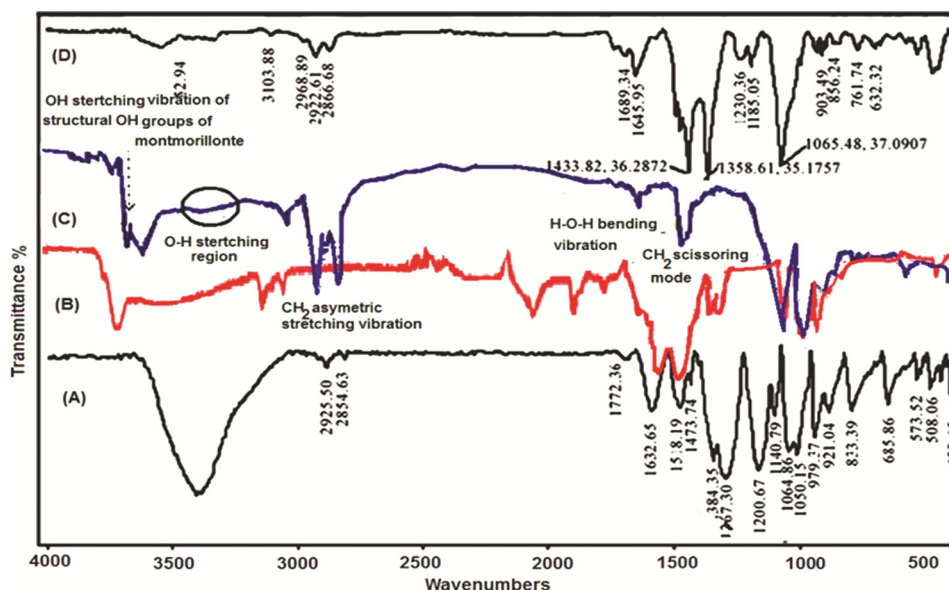


Fig. 1 — FTIR spectrums of (A) PEDOT, (B) Maghnite-TBA, (C)Maghnite-CTA, (D) PEDOT/Mag-CTA% nanocomposite.

CH₂, CH₃⁺ and CH₃, respectively. The IR spectra in Figs 1(B) and 1(C), show features that combine the specific groups of the montmorillonite and the CTAB or TBA molecule. The vibrations at 1183, 1141 and 1080 cm⁻¹ originate from the stretching of the C-O-C bond in the ethylenedioxy group and the C-S bonds in the thiophene ring. The FTIR spectra of PEDOT/Mag-CTA composite (Fig. 1(D)), exhibited a first peak shift related to the thiophene ring passing from 1309 to 1320 cm⁻¹, and a second peak shift corresponding to the C-O-C bond passing from 1183 to 1205 cm⁻¹. The reason for this shift can be referred to the interaction between the PEDOT polymer and the Maghnite-CTA. On the other hand, it can be seen from Fig. 1(D), that the Si-O stretching vibration at 1048 cm⁻¹ reveals the vertical attenuation of the spacer layer. This leads to the conclusion that EDOT has been effectively polymerized and inserted in the interlayer of organoclays, resulting in an increase in the interlayer space and a decrease in the number of Si-O. The small peaks between 2854 and 2925 cm⁻¹ can be ascribed to the CH elongations of ethylene in the thiophene ring. The FTIR peaks observed in the nanocomposites, when compared to the unmodified clays and those of PEDOT, demonstrated the presence of PEDOT in the nanocomposites. The same results have been found by Sariođlan²¹.

X-ray Diffraction analysis

The X-ray diffraction pattern of the maghnite, treated with NaCl (Mag-Na⁺), is shown in Fig. 2. It could be seen from Fig. 2, the presence of the peak

characteristic of the plane (001) of Maghnite clay at 2θ angle equal to 5.5°. The interlayer space in the mineral clay is then calculated to be 12.7Å. This finding can be explained by the fact that during the ion exchange process of Mag-Na⁺ with the cationic part of the surfactants "TBA⁺ and CTA⁺", each organic cation has been effectively inserted in the maghnite galleries. Indeed, during the cationic exchange of Mag-Na⁺ by TBA⁺ ions for a concentration level corresponding to 1CEC, the (001) reflection has been shifted from 2θ = 5.5° (d₀₀₁ = 12.7Å) for Mag-Na⁺ to 2θ = 3.0° (d₀₀₁ = 18.16Å) in the case of Mag-TBA. While for Mag-CTA with a concentration level of 2CEC, the XRD analysis revealed two peaks at 2θ = 4.5° and 2θ = 2.3° before and after cationic exchange, which give interlayer spaces of 19.27 Å and 33.53 Å, respectively. The incorporation of TBA⁺ and CTA⁺ ions into the clay galleries has been resulted in the increase of relative peak intensities corresponding to the (001) plane. Based on the XRD results, the detection of two signals instead of one in the Mag-CTA could be related to the diffraction of planes other than the d₀₀₁, which means the establishment of high order of regularity in the modified Maghnite²².

Figure 3 shows the XRD patterns of PEDOT /Mag-TBA nanocomposites containing (1,3,5 and 7wt%) of organoclay. The diffractograms of the PEDOT/Mag-TBA nanocomposites (1,3 and 5wt%) indicate that the obtained structure is exfoliated, this result is demonstrated by the absence of the diffraction peaks in the region of low angles. The PEDOT/Mag-TBA

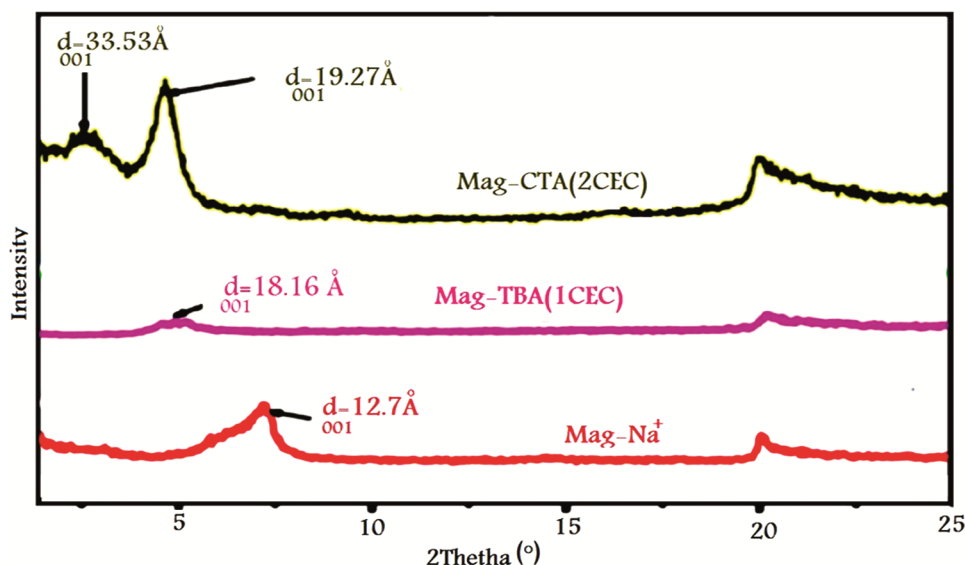


Fig. 2 — XRD patterns of the Maghnite-Na⁺, Maghnite-TBA(1CEC) and Maghnite-CTA (2CEC)

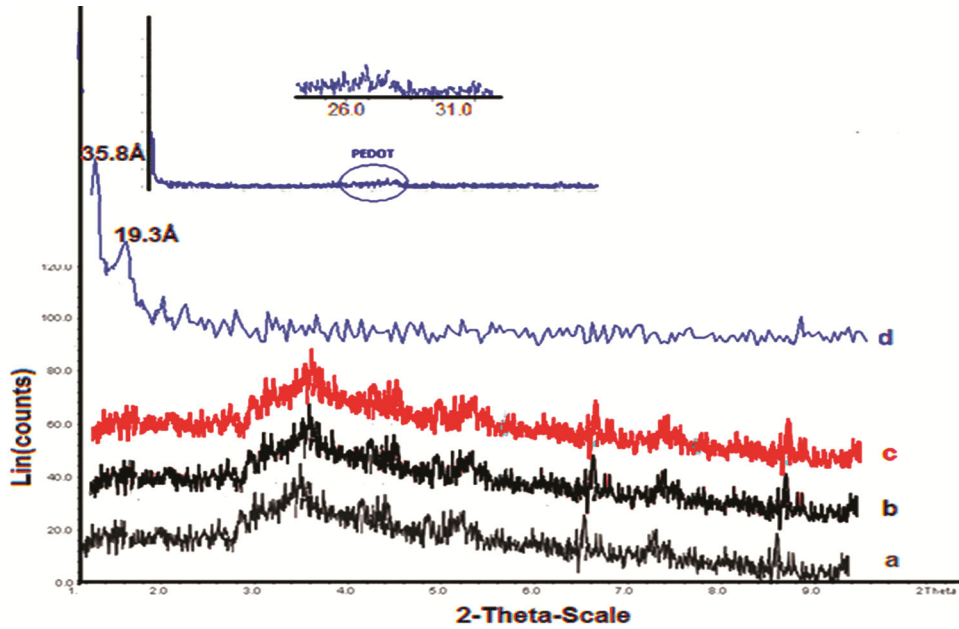


Fig. 3 — XRD patterns of Mag-TBA and (a) PEDOT/Mag-TBA1%, (b) PEDOT/Mag-TBA3%, PEDOT/Mag-TBA5% , (d) PEDOT/Mag-TBA7% nanocomposites.

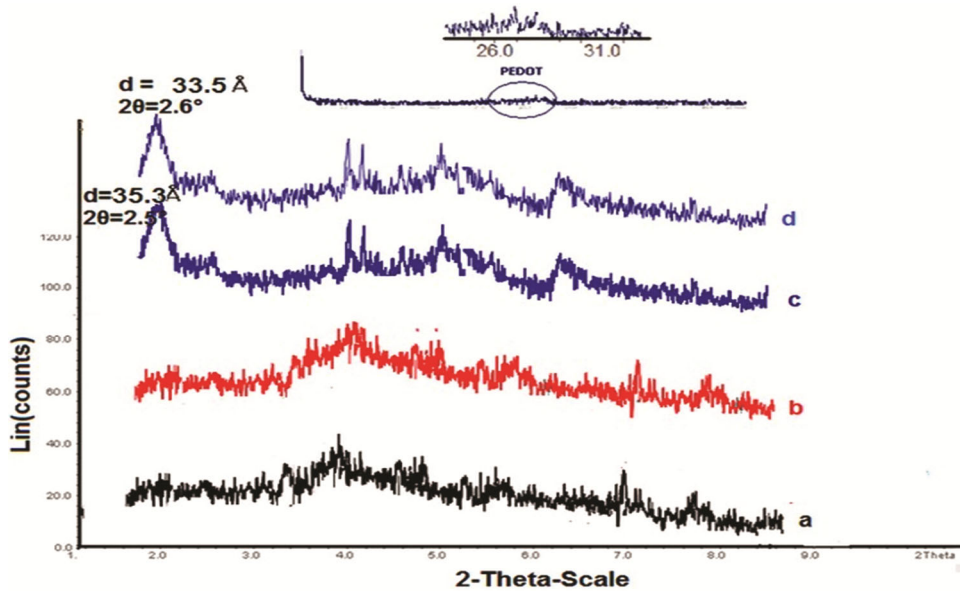


Fig. 4 — XRD patterns of Mag-CTA and (a) PEDOT/Mag-CTA3% (b) PEDOT/Mag-CTA5% PEDOT/Mag-CTA7% and (d) PEDOT/Mag-CTA10% nanocomposites.

nanocomposite with percentage weight of 7% exhibits two peaks. The first peak at $2\theta = 2.7^\circ$ corresponds to the polymer intercalation in the basal spacing of the clay with a distance of $d_{001} = 35.8 \text{ \AA}$, the second peak at $2\theta = 4.7^\circ$ having a distance $d_{001} = 17.3 \text{ \AA}$ corresponds to the rest of the non-intercalated maghnite. The d_{001} interlayer space of the nanocomposite has almost doubled compared to Mag-TBA (1CEC).

This result can be explained by the formation of an intercalated/exfoliated mixture. As can be seen from Fig. 4, the absence of the diffraction peaks at the low 2θ angles for PEDOT/Mag-CTA (3wt%) nanocomposite given indication of the formation of exfoliated morphology. The PEDOT/Mag-CTA nanocomposites of 5 and 7% by weight showed a displacement of the basal peak distance d_{001} at small

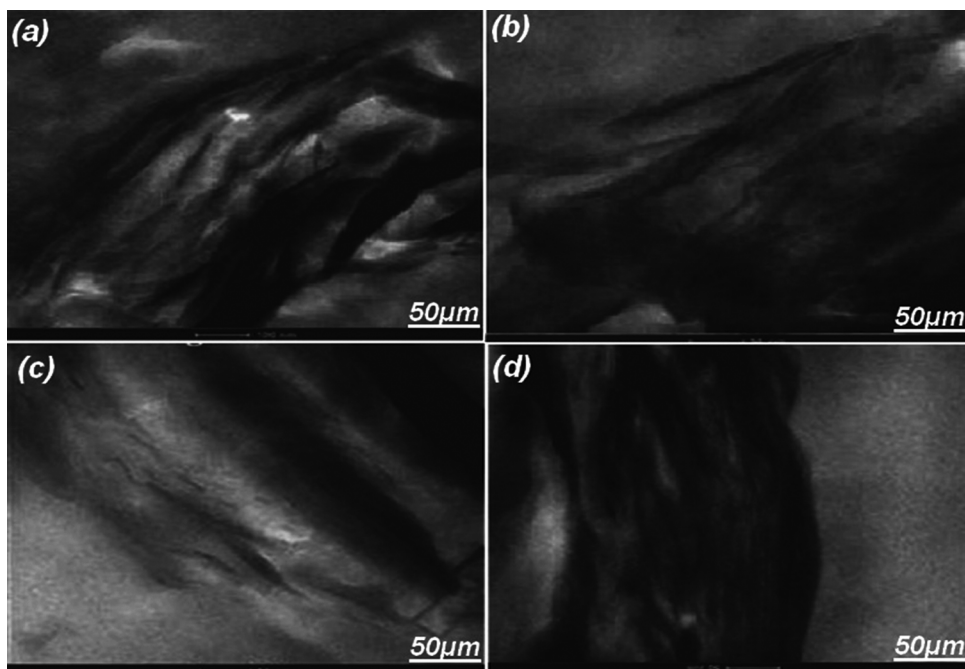


Fig. 5 — TEM images of: (a) PEDOT/Mag-TBA1% (Exfoliated), (b) PEDOT/Mag-TBA3% (Exfoliated), (c) PEDOT/Mag-TBA5% (exfoliated/), (d) PEDOT/Mag-TBA7% (exfoliated/intercalated structures) nanocomposites.

2θ angles between 2.6 and 2.5° corresponding to the distance $d_{001} = 35.3\text{A}$ and 33.5A , respectively. The peak around 2θ angles between 5.1° and 4.9° giving the following distances $d_{001}=18.83\text{\AA}$ and 18.52\AA , respectively. This finding clearly confirms that a part of the clay was exfoliated and then intercalated/exfoliated mixture morphologies were obtained. In the case of PEDOT/Mag-CTA (10%), the interfoliar distance corresponding to the (001) plane has a value of 25.5\AA , gives indication that the intercalated structure was formed. The increase in the basal spacing of Mag-CTA after in situ polymerization of EDOT, proved the existence of polymer chains between the intermediate layers of the clay.

Transmission Electron Microscopy analysis

TEM images of PEDOT/Mag-TBA(1CEC) nanocomposites containing 1,3,5 and 7% by weight of Mag-TBA are shown in Fig. 5. The dark lines in Fig. 5 indicate the nanolayers of nanocomposites on the polymer matrix. In Fig. 5(d), the TEM image of the PEDOT/Mag-TBA (7%) nanocomposite has exhibited a morphology formed of intercalated/exfoliated mixture. In Fig. 5(a),(b),(c), the TEM image of PEDOT/Mag-TBA nanocomposites (1.3 and 5wt%) shows exfoliated morphology. The results provided by the TEM analysis confirmed the dispersion of the polymer from the matrix into the organoclay sheets.

TEM images of PEDOT/Mag-CTA nanocomposites containing 3,5,7 and 10% by weight of Mag-CTA are depicted in Fig. 6. As can be seen from Fig. 6 (a), exfoliated structures were observed in the matrix PEDOT, demonstrating a high degree of exfoliation and that the clay layers are dispersed in the matrix. The PEDOT/Mag-CTA (3%) nanocomposite shows some disorder in the morphology of the clay. Contrary to the result in Fig. 6(b),(c), the TEM images of the PEDOT/Mag-CTA nanocomposites show an intercalated/exfoliated mixture morphology. While large clusters are clearly observable in PEDOT/Mag-CTA (10%), which can be explained by the fact that at high clay content there are immiscible zones between the clay and the polymeric matrix. Finally, the results obtained by TEM analysis are in good agreement with the XRD analysis.

Scanning Electron Microscopy analysis

Figure 7 shows the SEM photographs of the surface morphologies of the synthesized PEDOT/Mag-TBA nanocomposites. It was clearly observed that the PEDOT chains are not only formed inside the clay spaces, they are also found on the surface of clay particles. In Fig.7(a, b, c), the morphology of the composites had a spherical shaped structure, indicating uniform surface morphology. It is also shown for 7wt% clay, the PEDOT is in the form of a

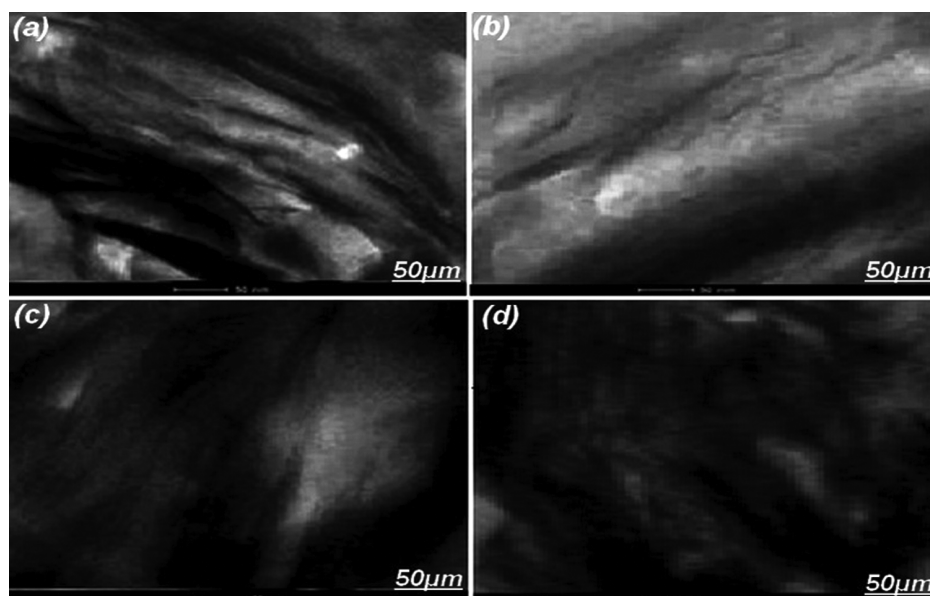


Fig. 6 — TEM images of: (a) PEDOT/Mag-CTA3% (Exfoliated), (b) PEDOT/Mag-CTA5% (exfoliated/intercalated structures), (c) PEDOT/Mag-CTA7% (exfoliated/intercalated structures), and (d) PEDOT/Mag-CTA10% (exfoliated/intercalated structures) nanocomposites.

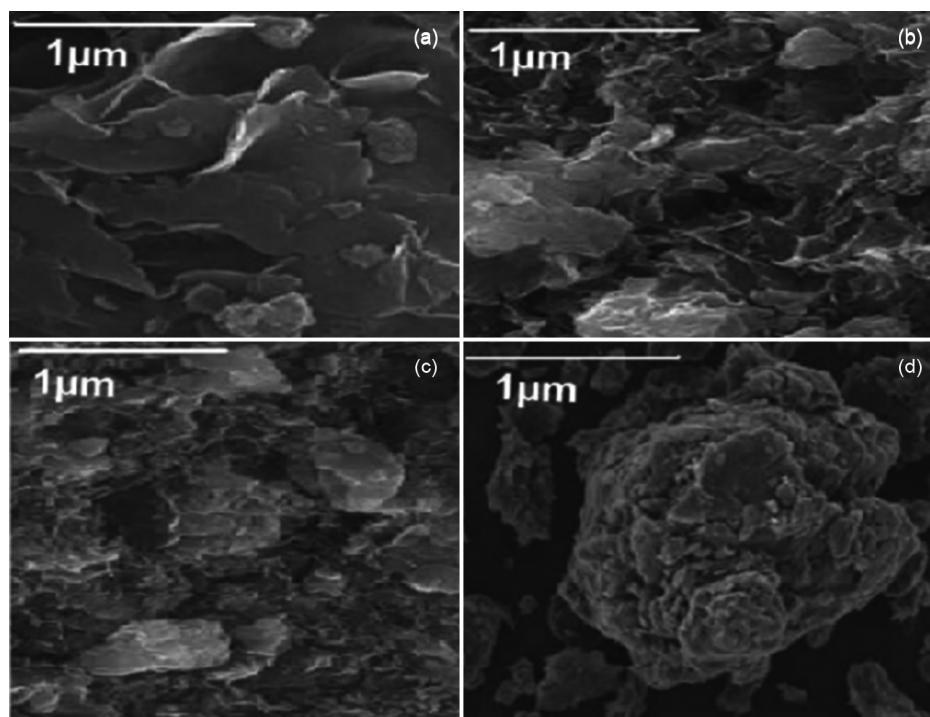


Fig. 7 — SEM images of: (a) PEDOT/Mag-TBA1%, (b) PEDOT/Mag-TBA3%, PEDOT/Mag-TBA5% , and (d) PEDOT/Mag-TBA7%nanocomposites.

"cauliflower". The nanocomposites containing 7wt% organoclay are more granular than those containing 1,3, 5wt% , thus resulting in a less porous and a more compact structure.

The SEM photographs of PEDOT/Mag-CTA nanocomposites are illustrated in the Fig. 8. The

analysis has shown that the nanocomposite becomes more irregular and porous when greater amount of organoclay dispersed in the PEDOT matrix. The micrographs in Figs 8 (a), (b) and (c) show more ordered and denser structures . The high content of the organoclay in the nanocomposites increase the

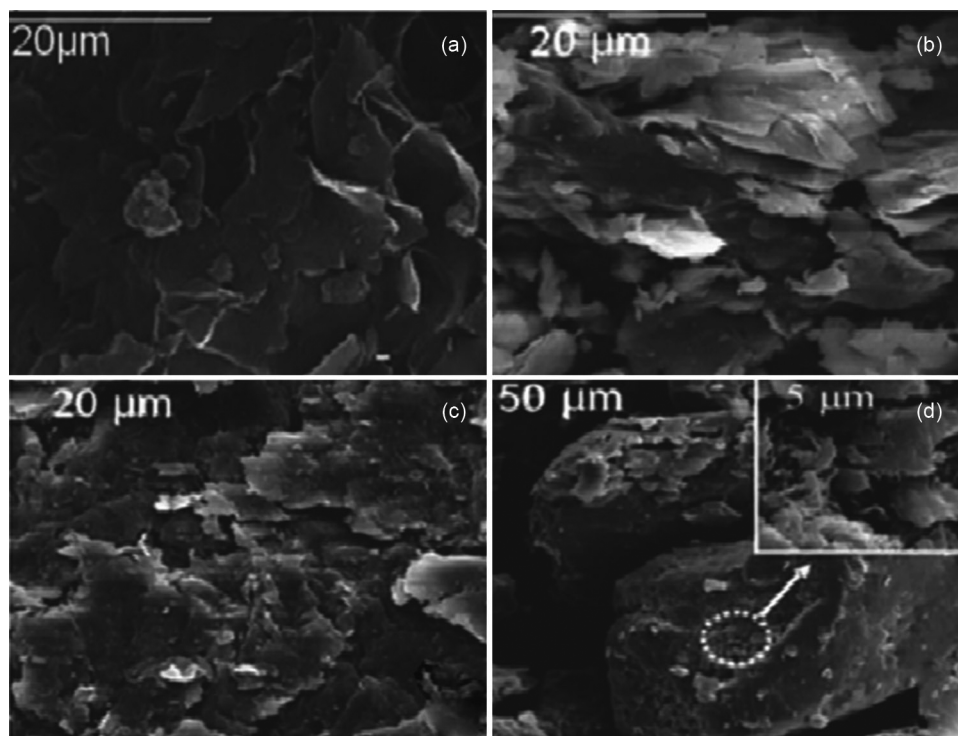


Fig. 8 — SEM images of: (a) PEDOT/Mag-CTA3%, (b) P PEDOT/Mag-CTA5%, PEDOT/Mag-CTA7%, and (d) PEDOT/Mag-CTA10% nanocomposites.

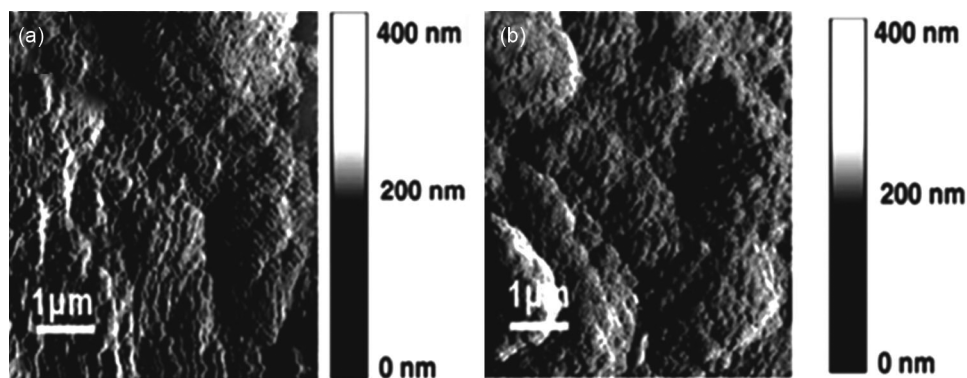


Fig. 9 — AFM images of PEDOT pure (a) and PEDOT/ Maghnite-CTA wt% (b) films.

compactness of the samples which become denser²³. It can be seen also that the PEDOT is in the form of non-uniformly distributed agglomerates.

Atomic Force Microscopy analysis

The average thickness ($\bar{\Gamma}$) and average RMS roughness (R) measured for the PEDOT polymer and the PEDOT/Mag-CTA nanocomposites are collected in Table 2. The morphology analyzed was centered on PEDOT and PEDOT/Mag-CTA with a weight ratio of 5wt%, which is more representative of the behavior of the nanocomposites. The AFM image of the surface of the PEDOT is relatively rough, this can be related

to the inhomogeneous structure of the material (Fig. 9). The surface appeared agglomerated with irregular form. However, a drastic change in the morphology has been observed in the sample incorporated with 5wt% Mag-CTA. The surface takes on a more harmonious form, with a reduction of the irregularities of the agglomerations. The Table 2 shows a significant decrease in R from 153 nm to 112 nm before and after 5wt% Mag-CTA is incorporated in the synthesis of the nanocomposite, this decrease was also observed in the case of heterocyclic conductive polymers, especially polypyrrole^{24,25}.

Thermogravimetric analysis

Thermogravimetric analysis (TGA) and differential thermal analysis (DTG) of the samples were performed under a nitrogen atmosphere between room temperature and 900°C. Results are presented Figs 10 (a) and 10 (b). In Fig. 10 (a) the TGA curves of PEDOT/Mag-TBA nanocomposites displays two well defined events of weight loss : an initial weight loss is recorded with the PEDOT at approximately 305°C, which changes to 375°C with the nanocomposite PEDOT/Mag-TBA, the second weight loss is

observed between 600 and 700°C is due to the dehydroxylation of the silicate structure. The thermal stability of the PEDOT matrix has been improved with increasing Mag-TBA content in the polymer. According to Fig. 10 (a), the high thermal stability was observed in the nanocomposite with 5wt% modified clay. While for nanocomposite 7wt% exhibited lower temperature of decomposition than sample with 5wt%. The decrease in thermal stability can be attributed to the absorption of excessive amounts of Hydrogenure Tetrabutylammonium (TBAHS). Thus, the presence of rate content higher than 5wt% slows down the decomposition of the nanocomposites²⁶.

The results of TGA/DTG analysis for PEDOT/Mag-CTA x wt% nanocomposites are presented in Fig 11 and Table 3. According to Table 3, the first weight loss of about 2-3% is observed in all samples

Table 2 — Average thickness (l) and average RMS roughness (R) of PEDOT and PEDOT/Mag-CTA nanocomposites.

| Rate of clay (%) | l (lm) | R(nm) |
|--------------------|--------|-------|
| PEDOT | 0.86 | 155 |
| PEDOT/Mag-CTA3wt% | 0.95 | 121 |
| PEDOT/Mag-CTA5wt% | 1.08 | 117 |
| PEDOT/Mag-CTA10wt% | 1.33 | 109 |

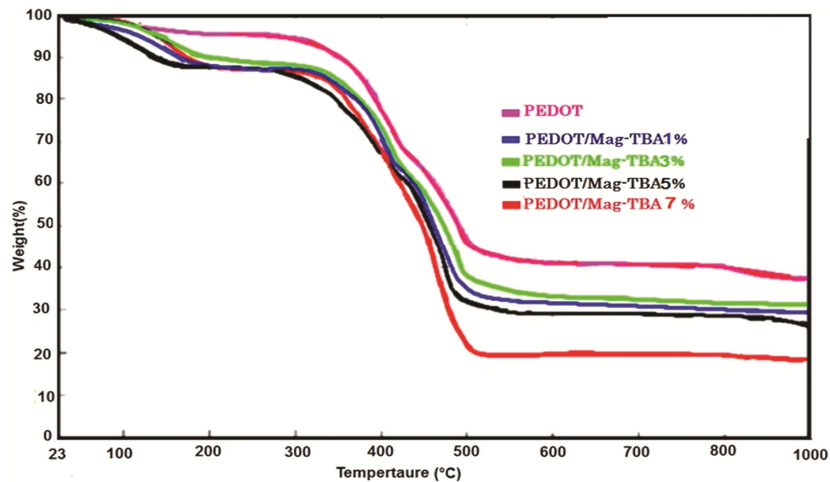


Fig. 10 — TGA curves of PEDOT pure and PEDOT Mag-TBAwt% nanocomposites.

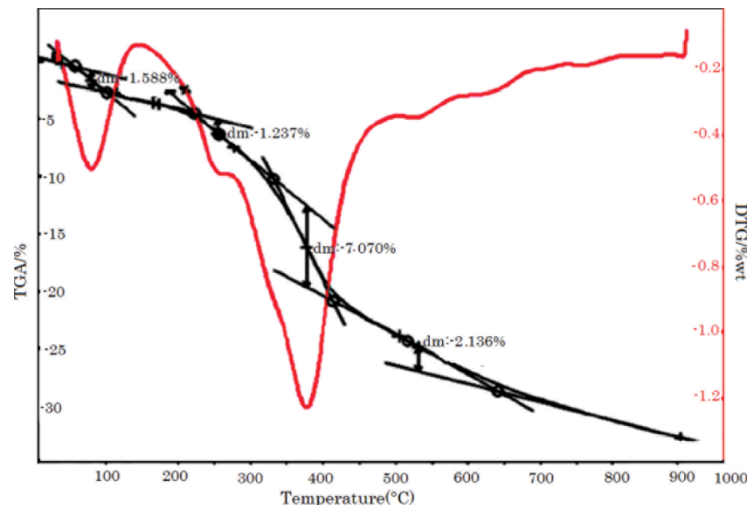


Fig. 11 — DTG curves of PEDOT /Mag-CTAwt%, nanocomposites

Table 3 — Degradation temperatures of pure PEDOT and PEDOT/Mag-CTA nanocomposites.

| Rate of clay (%) | Degradation temperature and mass losses | | | | | | | |
|------------------|---|-----|-------------------------|-----|-------------------------|-----|-------------------------|-----|
| | 1 st bearing | | 2 nd bearing | | 3 rd bearing | | 4 rd bearing | |
| | T (°C) | dm% | T (°C) | dm% | T (°C) | dm% | T (°C) | dm% |
| PEDOT | | | 150-176 | | 332-350 | | - | - |
| PEDOT/MagCTA3% | 62 -107 | 2.2 | 201-241 | 3.2 | 314-398 | 11 | 501-648 | 1.5 |
| PEDOT/MagCTA5% | 64 -109 | 3 | 217-260 | 1.3 | 325 -409 | 7 | 508-651 | 2 |
| PEDOT/MagCTA7% | 51-96 | 1,6 | 219-250 | 1.5 | 317-396 | 15 | 506 -635 | 3 |

Table 4 — Variation of electrical conductivity as a function of the amount of Maghnite-CTA.

| Sample | Molar of EDOT | Mag-CTA% | Electrical conductivity (Scm ⁻¹) |
|--------------------|---------------|----------|---|
| PEDOT/Mag-CTA1wt% | 0.05 | 1% | 2,3 10 ⁻³ |
| PEDOT/Mag-CTA3wt% | 0.05 | 3% | 1,9 10 ⁻³ |
| PEDOT/Mag-CTA5wt% | 0.05 | 5% | 1,1 10 ⁻³ |
| PEDOT/Mag-CTA10wt% | 0.05 | 10% | 0,46 10 ⁻³ |

around 100°C. This loss is due to the evaporation of hygroscopic water. The main mass losses in nanocomposites correspond to the decomposition of the PEDOT matrix of which, the temperatures of the 3rd palier are much higher than those of pure PEDOT, whose decomposition starts at about 150°C. The recorded mass losses of nanocomposites are therefore more thermally stable than pure PEDOT. In the last weight loss of 1-3% in the temperature range 700-900°C, the water structure is liberated by the decomposition of the bound hydroxyl groups²⁷. The results obtained showed that the amount of organic clay required to prepare a nanocomposite with high thermal stability is 3wt% in the case of Mag-CTA.

Conductivity

The conductivity of the nanocomposites was measured according to the four-tip on-line method. The results obtained from the variation in electrical conductivity are shown in Table 4. The resistivity ρ (Ω) of the pellet sample was calculated according to the following equation: ρ (Ω) = $\mathbf{R.I.C_f}$, where R is the resistance, I is the thickness of the pellet and C_f is the device correction factor = 4.53. The obtained conductivities vary between 2.3×10^{-3} and 0.46×10^{-3} Scm⁻¹. The result shows that all synthesized composites behave as semiconductors. The drop in conductivity after clay incorporation can be explained by the fact that the clay particles act as a barrier for electrons mobility.

Conclusion

The polymer (PEDOT) clay Maghnite nanocomposites have been prepared by in situ polymerization of EDOT monomer in the interlayer

space of surfactant modified clay. The synthesis was assisted by ultrasonic method. The nanocomposites have been characterized by different techniques like: XRD, FTIR, AFM, TGA, SEM and TEM. The IR spectroscopic study showed that the characteristic bands of poly(3,4-ethylenedioxythiophene) matrix and the organoclays are presented in the nanocomposites. The structural study of PEDOT/Mag-TBA nanocomposites with loading rates below 7 wt%, shows the existence of exfoliated morphologies. Results of X-ray diffraction and analysis of TEM images of PEDOT/Mag-CTA nanocomposites greater than 3wt% , revealed that the morphology of the nanocomposites obtained is characterized by an intercalated/exfoliated mixture , causing an expansion of the space between the layers. In the AFM analysis, the results show a drastic change in the topographical image induced by the incorporation of 5wt% of organoclay in the nanocomposite. Results obtained according to TGA approved that the best amount of organoclay required to prepare a nanocomposite poly(3,4-ethylenedioxythiophene)/Mag-TBA with high thermal stability is 5 wt% of the organoclay, while for PEDOT/Mag-CTA nanocomposite the best amount is 3wt%. Electrical conductivity measurements showed a decrease in conductivity with increasing the content of organoclay since the later hinders the electron mobility over the nanocomposite.

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