

Spectroscopic Characterization of a New Type of Conducting Polymer–Clay Nanocomposite

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Introduction. The conductivity of a conducting polymer depends strongly on the arrangement of its chains.^{1,2} One way to improve the bulk properties of a polymer is to confine it in nanoscale environments. Nanocomposites are multiphase materials with two or more different compounds organized in the nanometer regime and can show electronic, mechanical, magnetic, and optical properties that are not present in the individual phases, but the basic reason for this synergism is not yet completely understood.^{3,4} Nanocomposites formed with inorganic host structures and polyaniline have been one of the most studied systems.^{5,6} In such systems, the polymeric chains are reasonably isolated from one another by the inorganic structure, providing an unique opportunity to explore spectroscopic properties of single chains intercalated in a rigid matrix.⁷ FTIR, EPR, and other techniques have been largely used to characterize these complex systems.^{5–7} Among the inorganic hosts employed to confine conducting polymers, clays are frequently used.^{5,6,8} There are several works in the literature using different synthetic strategies to prepare polyaniline between the layers of montmorillonite, a natural clay,^{9–13} and according to the authors, the emeraldine salt form of polyaniline (ES–PANI) is then formed. Up to now, Raman spectroscopy has been little explored to investigate the nature of these types of hybrid materials. In this work, we present for the first time the resonance Raman (RR) characterization of a polymer–clay nanocomposite formed by the aniline polymerization in the presence of smectite clay Swy2 montmorillonite (MMT) using two different synthetic routes reported in the literature.^{9,11} One of these routes leads to ES–PANI while the other leads to a new type of conducting polymer–clay nanocomposite.

Experimental Section. (a) Preparation of Polymer–Clay Nanocomposites by In Situ Polymerization. Swy2 montmorillonite (MMT, from Clay Minerals Research) was treated with sodium chloride and size fractionated to obtain the homoionic Na⁺-form free of main impurities. The acetate method was used to determine the cationic exchange capacity of MMT (45 mmol/100 g of clay). The following experimental procedure was adapted from ref 11. Then 230 mL of an aqueous suspension of 2.6 g of MMT was thermostated at 80 °C and then dropped slowly into 20 mL of a 0.16 mol/L solution containing aniline (Merck, previously distilled under vacuum) and 0.3 mol/L HCl (Merck). After being stirred for 6 h at 80 °C, the suspension was filtrated and the clay was washed with deionized water up to the elimination of nonintercalated anilinium ions. The anilinium–clay material (An⁺–MMT) was resuspended in 100 mL of deionized water and 20 mL of suspension was used in the polymerization experiment

as follows: deionized water was added to the suspension up to the final volume of 100 mL; the pH was adjusted to 2 with HCl solution, and then 1 mmol of ammonium persulfate (Merck) was added. After 12 h a dark green solid was isolated by filtration and dried in a desiccator.

(b) Preparation of Polymer–Clay Nanocomposites by ex Situ Polymerization. An aqueous suspension containing 0.01 g/100 mL of Na⁺–MMT was prepared and sonicated in an ultrasonic bath for 1 h to cause the interlayer swelling and the clay exfoliation/delamination. Then 75 mL of this Na⁺–MMT suspension and 25 mL of a solution containing 1 mol/L camphorsulfonic acid, CSA, (Merck) and 0.5 mol/L aniline were mixed by stirring at room temperature, and then 2.85 g of ammonium persulfate was slowly added to the suspension. The reactional mixture was maintained under stirring for 10 h. The green composite particles were isolated by filtering and dried. The general procedure reported above was described in refs 9 and 10.

The resonance Raman spectra with 632.8 and 488.0 nm exciting radiations were recorded in a Renishaw Raman imaging microscope (system 3000) containing an Olympus metallurgical microscope and a CCD detector. The laser beam was focused on the sample in a ca. 1 μ m spot by an $\times 80$ lens. Laser power was always kept below 0.7 mW at the sample, aiming to avoid its degradation. The FTIR spectra were obtained using a BOMEM MB-100 instrument and the samples dispersed in a KBr pellet. X-ray powder diffraction patterns were obtained in a Phillips MPD-1880 diffractometer with Cu K α radiation. EPR spectra were recorded at room temperature from powders on a Bruker ER 200 spectrometer operating in the X-band (~ 9.5 GHz). UV–vis–NIR spectra of the samples were obtained from aqueous suspension in a Hewlett-Packard 2583 diode array spectrophotometer. Resistivity measurements of powders were performed by the two points method using an impedance analyzer Autolab PGSTAT30 (Ecochemie) with FRA module. A dc potential of 0.0V with a modulation of 5 mV (rms) was imposed in the 10 kHz to 10 mHz frequency range.

Results and Discussion. XRD was used to follow anilinium intercalation and polymerization during the in situ polymerization. The d_{001} diffraction peak was found at 12.8 (Na⁺–MMT), 13.5 (anilinium–MMT) and 13.2 Å (polymer–MMT). Taking into account a clay thickness of 9.6 Å, the basal spacing of 13.2 Å corresponds to a gallery height of 3.6 Å. Similar value has been found by others authors in a similar system,^{14,15} confirming the polymer intercalation. The X-ray diffraction pattern of the product formed by ex situ polymerization did not show distinct peaks, suggesting that the clay layers were chaotically dispersed in the polymeric structure.

UV–vis–NIR spectra of polymer–MMT samples obtained from the two routes, of polyaniline as emeraldine salt (ES–PANI) and of anilinium–MMT are presented in Figure 1. The ES–PANI spectrum is very similar to the one obtained from the polymer–MMT prepared by ex situ polymerization and presents the same main features: a peak at 450 nm and the broad band starting at ca. 600 nm and decreasing at 1050 nm. The spectrum of the polymer–MMT obtained by in situ polymerization

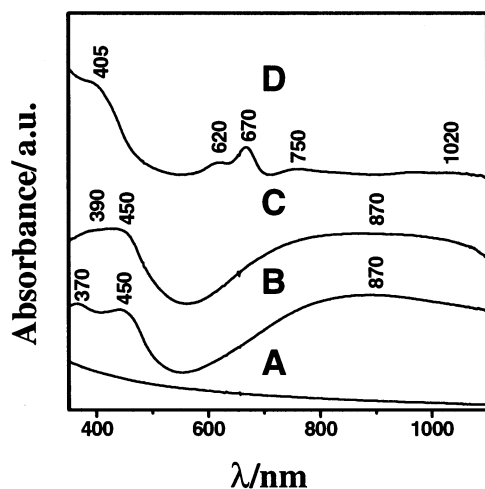


Figure 1. UV-vis-NIR spectra of: aqueous suspension of anilinium-MMT (A), ES-PANI dissolved in *N*-methyl pyrrolidone (B), and an aqueous suspension of polymer-MMT samples prepared from ex situ polymerization (C) and in situ polymerization (D).

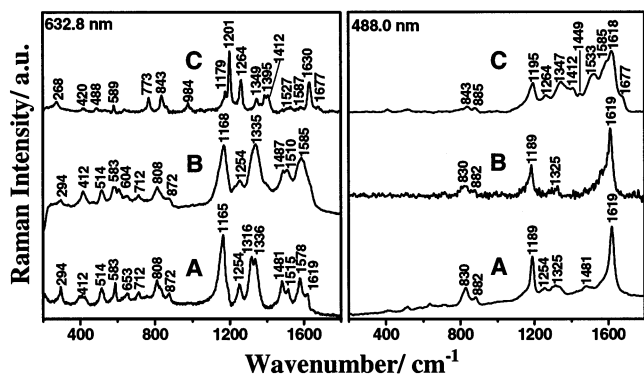


Figure 2. Resonance Raman spectra excited at 632.8 and 488.0 nm of powdered samples of ES-PANI (A) and polymer-MMT samples prepared from ex situ polymerization (B) and in situ polymerization (C).

shows absorption bands at 405, 620, 670, and 750 nm (not observed in the anilinium-MMT spectrum), which are assigned to localized transitions, and a tail of an absorption band in the NIR region, which can be attributed to free charge carriers.¹⁶

Figure 2 shows the RR spectra of the green polymer-MMT samples and the ES-PANI, using two exciting radiations. The spectra of polymer-MMT obtained by ex situ polymerization are very similar to those of ES-PANI for both exciting radiations. At 632.8 nm excitation, the bands at 1316 and 1336 cm^{-1} in the ES-PANI spectrum correspond to the unresolved band at 1335 cm^{-1} in the polymer spectrum and are characteristic of radical cation segments of ES-PANI. The spectrum of the polymer-MMT formed by ex situ polymerization at 488.0 nm excitation shows characteristic bands of the reduced units of ES-PANI. This result and the UV-vis-NIR data show that the polymer prepared by ex situ polymerization is ES-PANI.

The resonance Raman spectrum of the green polymer-MMT prepared by in situ polymerization and excited at 632.8 nm is very different from the ES-PANI spectrum. The bands at 984, 1179, 1201, 1264, 1349, and 1395 cm^{-1} can be associated with the bands at 990, 1175, 1200, 1270, 1320, and 1380 cm^{-1} observed in the spectra of poly(diphenylamine) excited at 632.8 and 514.5 nm.¹⁷ This correspondence suggests the presence

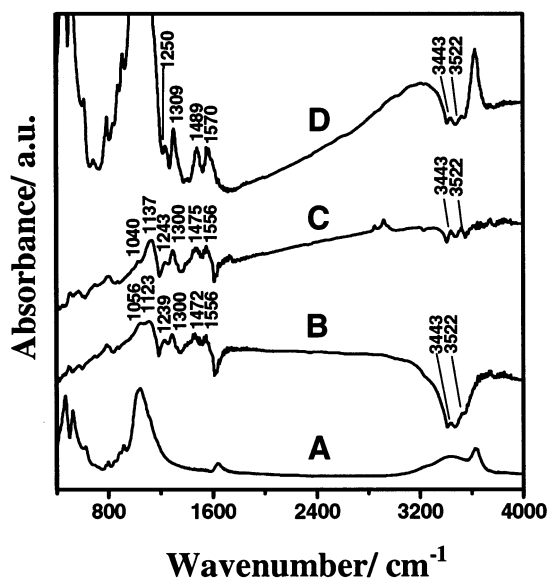


Figure 3. FTIR spectra in absorbance of Na^+ -MMT (A), ES-PANI (B), and polymer-MMT samples prepared from ex situ polymerization (C) and in situ polymerization (D).

of radical and quinoid segments of benzidine in the structure of the synthesized polymer, indicating that intercalated anilinium species are involved in a tail to tail polymerization. The formation of 4,4'-disubstituted biphenyl compounds in montmorillonite has been demonstrated in a systematic study by Soma et al.,¹⁸ corroborating our description of the main polymeric chain. Nevertheless the RR spectrum at 488.0 nm shows bands at 1195 and 1618 cm^{-1} that can be assigned to reduced benzenoid segments of PANI polymer, indicating that a head to tail polymerization occurred as well. So, if the polymeric chain is formed by two kinds of segments, benzidine and *p*-diaminobenzene, the intercalated polymer main chain must have an azo-type bonding, what is confirmed by the bands at 1412 and 1449 cm^{-1} observed in the RR spectrum excited at 488 nm. These bands appear with high intensity in the RR spectrum of intercalated poly(benzidine)-MMT (not shown). The formation of $\text{N}=\text{N}$ azo segments by polymerization of aniline adsorbed in Fe-montmorillonite has been suggested by Soma and Soma.¹⁹

Figure 3 shows the Na^+ -MMT and ES-PANI FTIR spectra, together with those of the polymer-MMT nanocomposites. In the spectra of polymer-MMT obtained by in situ polymerization, the spectral region near 1100 cm^{-1} is dominated by clay bands and the bands in the 3700–3000 cm^{-1} region and at 1630 cm^{-1} , assigned to adsorbed water and structural clay OH.²⁰ There is no significant difference between the IR bands of the polymers obtained by the two routes and these spectra are similar to the ES-PANI spectrum. The use of the IR information and of the color of the polymer-MMT nanocomposites can lead one to incorrectly interpret that ES-PANI is formed in the clay interlayer, as is frequently observed in the literature. This result is a clear evidence that RR spectroscopy is more sensitive than FTIR to characterize this type of systems.

Another evidence that the two intercalated polymers are different is given by their EPR spectra (Figure 4). There is practically no signal in the EPR spectrum of the polymer-MMT prepared by in situ polymerization while the EPR spectrum of the polymer-MMT obtained by ex situ polymerization shows a strong signal. Although

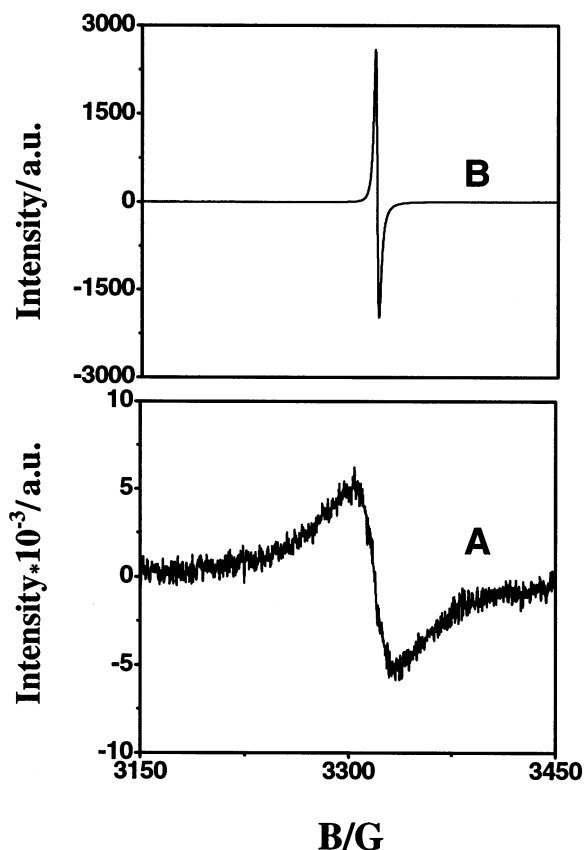


Figure 4. EPR spectra of polymer-MMT powdered samples prepared from in situ (A) and ex situ (B) polymerization.

the relative polymer/clay ratio is lower in the in situ polymerization than in the ex situ, the observed signal was so weak that can only be explained if a different polymeric chain was produced by the in situ polymerization.

The ac conductivity for the polymer-MMT sample synthesized by in situ polymerization is ca. $10^{-3} \text{ S} \cdot \text{cm}^{-1}$ that is similar to the value obtained by Wu et al.,¹¹ using the same route, and precludes the presence of dimer species or small oligomers into the clay, while on the other hand reinforcing the formation of a polymeric structure. The relatively high value of the conductivity, together with the weak EPR signal, suggest that in this intercalated polymer the conduction is via diamagnetic free carriers.

The polymer prepared through ex situ polymerization led to a conductivity value of $0.5 \text{ S} \cdot \text{cm}^{-1}$, which is consistent with the value obtained by other authors on similar systems using this route of polymerization^{9,10}

and is in agreement with the spectroscopic data that indicate the formation of ES-PANI.

In conclusion, for the first time it is demonstrated that the nanocomposite prepared by the aniline polymerization in montmorillonite according to the in situ polymerization is a polymer with tail-to-tail (benzidine) and head-to-tail (*p*-diaminobenzene) segments. The proposed polymeric structure here presented and supported by experimental evidences is clearly contrasting with previous results using other spectroscopic techniques,^{11–13} showing that the RR technique is a very powerful tool to study complex systems formed by conducting polymers and inorganic hosts.

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