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Two Spectroscopies as Main Source for Investigation of Polymer-Clay Materials

Gustavo Morari do Nascimento

Abstract

In the recent years the synthesis and characterization of nanomaterials has been one of the most efficacious way to produce new materials with improved or completely new properties. The polymer-clay nanocomposites are one of the most interesting nanomaterials with the possibility to create a myriad of new materials with many applications. Lamellar materials are classified as two-dimensional (2D), because there are formed by platelets piled up in one crystallographic direction, as the graphite and clays. The synthesis of controlled dimensional nanostructures as well as the characterization of the intrinsic and potentially peculiar properties of these nanostructures are central themes in nanoscience. The study of different nanostructures has great potential to test and understand fundamental concepts about the role of particle dimensionality on their physicochemical properties. Among the various materials studied in the literature, undoubtedly, polymer-clay materials, especially conducting polymers with smectite clays, such as montmoril-lonites (MMT) are of particular note. Our group have paid many efforts in the characterization of nanomaterials by using powerful spectroscopic techniques to study both the guest and host in case of inclusion compounds, nanofibers, carbon allotropes or many phases present in polymer-clay nanocomposites. There are two central questions that it was possible to address in this study: (i) the molecular structure of the polymer is drastically changed inside the interlayer cavity of clay and (ii) by using the appropriate synthetic or heating route is possible to change the molecular structure of the confined polymer. In the follow lines, it is briefly told the main aspects of resonance Raman and X-ray absorption spectroscopies in the study of polymer-clay nanocomposites.

Keywords: clay, nanocomposites, raman, XANES

1. Introduction

1.1 Clay science

Probably the clay is one of the most ancient and important material used and transformed by the humankind in order to produce a myriad of objects with many purposes. In fact, the historical impact of clay can be weighted by their intense use in many passages of one of the most influential book, the biblical text, as a synonym of a material that can be forged and transformed, as follows:

"Then the Lord God formed the man of dust from the ground and breathed into his nostrils the breath of life, and the man became a living creature." Genesis 2: 7 [1].

"But now, O Lord, you are our Father; we are the clay, and you are our potter; we are all the work of your hand." Isaiah 64: 8 [1].

In fact, farmers to produce plants explore the mechanical and chemical environment of clays, ceramists and artists continuously use clays to create extraordinary objects. To the editor, give softness to the paper surface in high quality prints. In medical area may be a relief for diarrhea and so on. In fact, there is no uniform nomenclature for clay and clay materials [2–4]. Clay material is "...a naturally occurring material composed primarily of fine-grained minerals, which is generally plastic at appropriate water contents and will harden with dried or fired". Naturally, this definition is elastic, because in geology science is considered clay the particles with size dimension of less than <4 μm, while in colloid science the value <1 μm is more acceptable [5]. The term clay mineral signifies a class of "...phyllosilicate minerals and minerals which impart plasticity to clay and which harden upon drying or firing" [6]. Since the origin of the mineral is not part of the definition, clay mineral (unlike clay) may be synthetic.

Hence, clay minerals have layers ordered in nanoscale and many different components can be present, as consequence, only by using advanced spectroscopic techniques it is possible to study their structures in detail. X-ray diffraction techniques are applied to determine the crystalline phases and basal distances d_{001}. The d_{001} is an important parameter to follow in the intercalation process. Clays layers have structures builded from tetrahedral sheets in which a silicon atom is surrounded by four oxygen atoms and octahedral sheets in which a metal like aluminum or magnesium is surrounded by eight oxygen atoms [7–10]. The tetrahedral (T) and octahedral (O) sheets are bonded by the oxygen atoms. Unshared oxygen atoms are present in hydroxyl form (see **Figure 1**). Two main arrangements of T and O layers can be observed in the structures of clays. One tetrahedral fused to one octahedral (1:1) is called as kaolin group with the general composition of $Al_2Si_2O_5(OH)_5$ and the layer thickness of ~0.7 nm. The crystal lattice consisted of one octahedral sheet
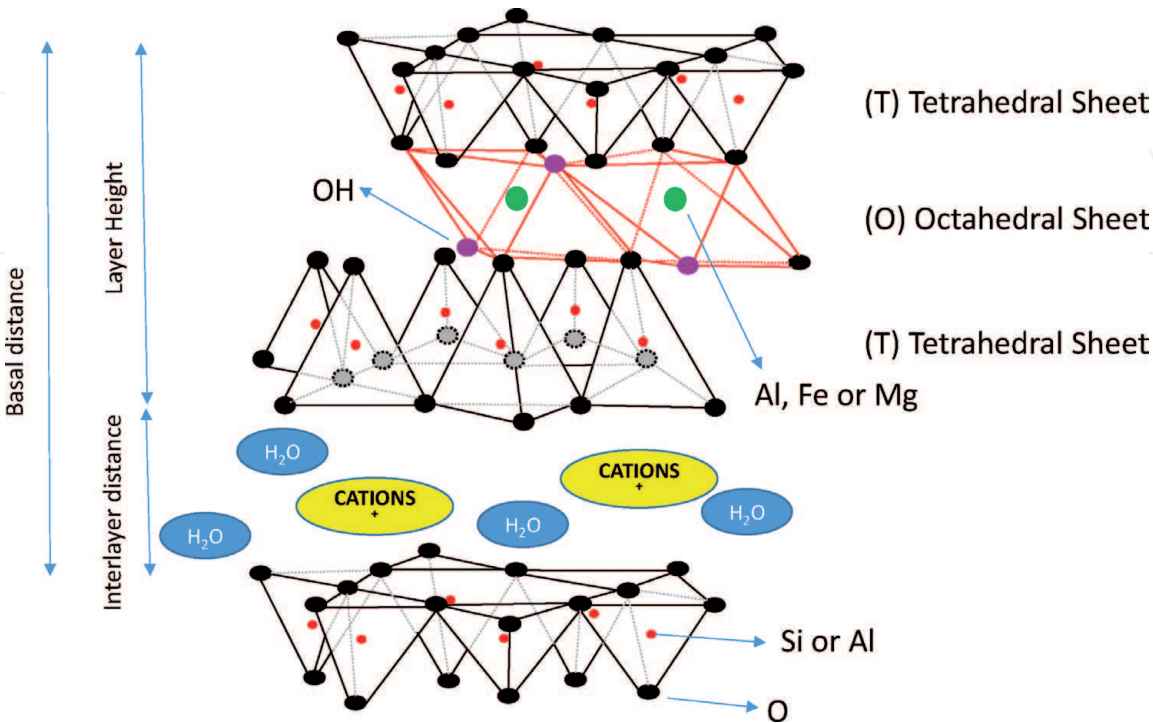

Figure 1.
Schematic representation of T:O:T structure of Smectite clay group.

sandwiched between two tetrahedral sheets (2:1) with the total thickness of 0.94 nm is well known as phyllosilicates. The 2:1 phyllosilicates those are electrostatically neutral with no inter layer ion and no expansion in water are known as pyrophyllite. However, when silicon in T sheets is substituted by aluminum, the 2:1 structure is called mica. The negative charge induced by this change is balanced by the introduction of potassium cations between the layers. Potassium cation has similar size of the hole created by Si/Al in tetrahedral sheets. Consequently, the 2:1 layers are held together strongly and the swelling or exfoliation of layers is not possible. The aluminum cations in the O layers can be partially substituted by divalent magnesium or iron cations in neutral pyrophyllite and as result the smectite clay group is formed, whose structure consists of a central sheet containing groups $MO_4(OH)_2$ of octahedral symmetry associated with two tetrahedral sheets (MO_4) producing layers designated T:O:T (see **Figure 1**). The O sites are occupied by ions of aluminum, iron and/or magnesium, while the centers accommodate tetrahedrons of silicon and aluminum ions.

In the last decades, the synthesis and characterization of nanomaterials and nanocomposites with improved or new properties has made the possibility of producing intelligent materials real [11]. One group of interesting nanomaterials with the possibility to create a myriad of new materials with many applications is the polymer-clay nanocomposites. Lamellar materials are classified as two-dimensional (2D), because there are formed by platelets piled up in one crystallographic direction, as the graphite and clays [12, 13]. The synthesis of controlled dimensional nanostructures as well as the characterization of the intrinsic and potentially peculiar properties of these nanostructures are central themes in nanoscience [14]. The study of different nanostructures has great potential to test and understand fundamental concepts about the role of particle dimensionality on their physicochemical properties. Among the various materials studied in the literature, undoubtedly, polymer-clay materials, especially conducting polymers with smectite clays, such as montmorillonites (MMT) are of particular note [15–25].

Our group have paid many efforts in the characterization of nanomaterials by using powerful spectroscopic techniques to study both the guest and host in case of inclusion compounds, [26] nanofibers, [27–29] carbon allotropes [30–38] or many phases present in polymer-clay nanocomposites [15–25]. In this brief chapter, we give an overview of some contribution of our studies of polymer-clay nanocomposites by using resonance Raman and X-ray absorption spectroscopies as main techniques of investigation. There are two central questions that was possible to address in our studies: (i) the molecular structure of the polymer is drastically changed inside the interlayer cavity of clay and (ii) by using the appropriate synthetic or heating route is possible to change the molecular structure of the confined polymer.

1.2 Techniques

1.2.1 Resonance Raman spectroscopy

Since the foundation of modern basis of physical sciences in the end of XIX century, the spectroscopies are essential to the investigation of the structure of the matter. The molecular spectroscopy are grounded in the studies of the transitions between the vibrational and/or rotational levels. Among the techniques that can be used to study the molecular structure, infrared and Raman spectroscopies are in a pivotal position. By using these techniques was possible the determination of structures from dyes [39], metallic complexes [40–42], conducting polymers [43, 44], polymer-clay nanocomposites [15–25] to carbon allotropes [30–38]. In Raman spectroscopy, [45–47] the physical phenomenon is very distinct from the infrared, which is a typical absorption

between allowed states, in the case of Raman; there is a scattering process of the incident radiation. The radiation source has much more energy than the vibrational transitions, but through the scattering process, it is possible to screen the vibrational levels (see **Figure 2**).

Another possibility in Raman spectroscopy is the use of different laser lines (E_0), as consequence there is the chance to probe electronic levels in addition to the vibrational ones. When the E_0 is equal or near to an electronic transition there is an increase of the Raman cross-section for at least 10^5 times and also the intensification of the vibrational modes associated to the chromophore structure. The use of microscopies coupled to the Raman instrument permits the investigation of the sample at microscopic level (or nanoscopic level if an electronic or probe microscopies were used) in a non-destructive manner. The main advantage however is the ability to focus the laser on a very small part of the sample (1 μm approximately or smaller). The high lateral resolution and depth of field (the order of a few micrometers) are very useful for the study of multilayered polymeric thin films or others complex materials, such as polymer-clay nanocomposites. In fact, the major part of our studies were conducted in a Raman instrument coupled with an optical microscopy.

1.2.2 X-ray absorption spectroscopy

There are many spectroscopic techniques employed routinely in clay science research in order to investigate multiple aspects of the samples. X-ray spectroscopy has a unique capability to obtain atom-specific information just by tune the correct incident energy of a synchrotron radiation ring. Hence, it is possible to study different atoms and their environments in a clay material or any other complex sample. An X-ray absorption spectrum (XAS) is a consequence of the excitations of a core electron to molecular unoccupied states (or extended states in a case of solid
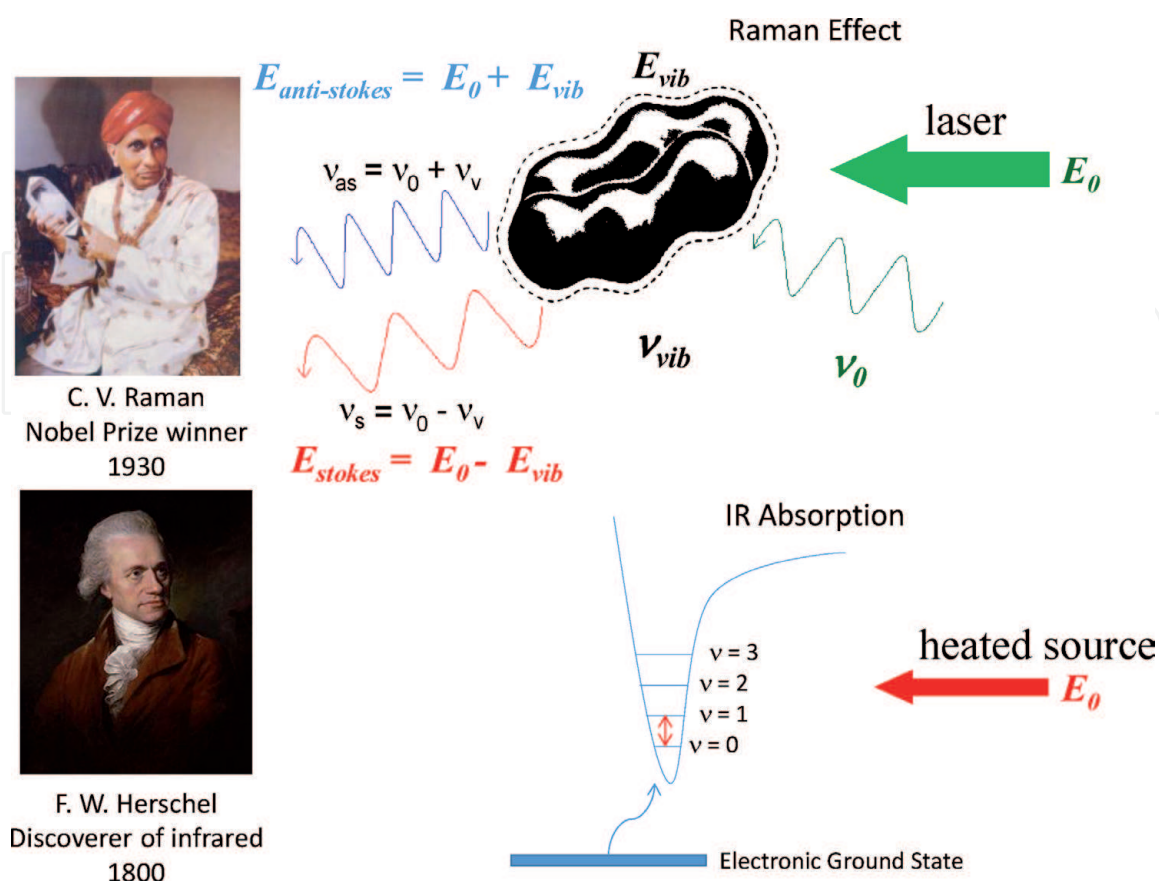

Figure 2.
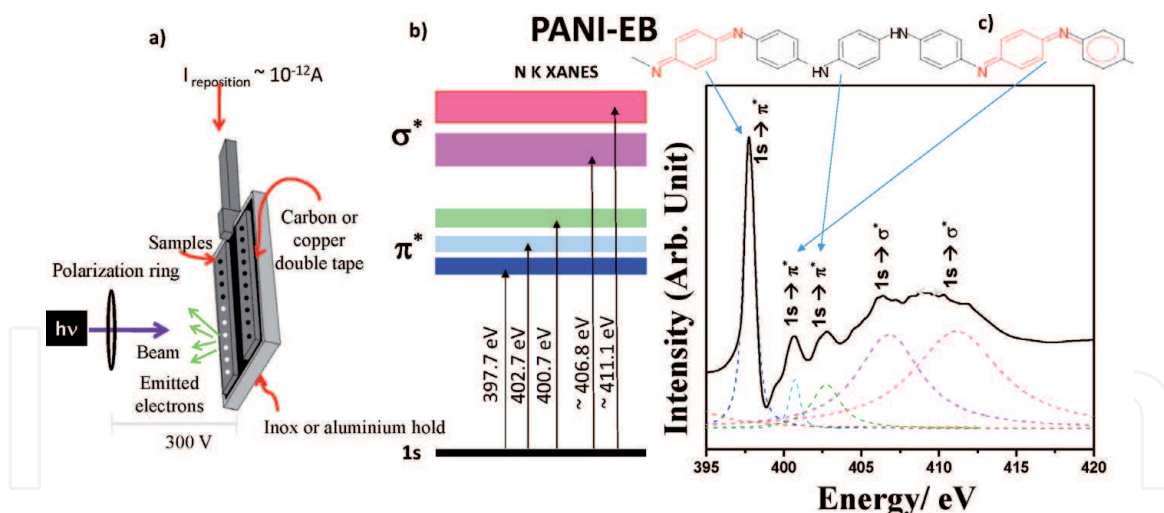*Schematic representation of Raman and IR phenomenon.*

Figure 3.
a) the N K XANES measurements are done in ultrahigh vacuum (the pressure inside the chamber is ca. 10^{-7} mbar). The measured signal is the current of reposition of electrons from the sample (near 10^{-12} a), after the X-ray absorption there are many emission effects (photoelectrons, electrons auger and secondary electrons) those are proportional to the absorption intensity [25]. The arrangement used in our experiments is displayed above. A grooved rod is placed over the main rod to delimit the area (ca. 0.2 cm^2) and prevent the mixing of the samples, since the measurements are made with the rod positioned vertically in the sample chamber. b) Schematic representation of the transitions from 1 s to π^* and σ^* states of a molecular material (PANI-EB), an the correspondent N K-edge X-ray absorption spectrum is also displayed. c) N K XANES spectrum of powered sample of PANI-EB is represented by the black top continuous line (—). The five Voigt bands used in the deconvolution of the experimental spectrum are shown below the experimental data (red dashed lines, – – –). The sum spectrum of the five Voigt bands is also displayed (red pointed line, $\cdots$). Scheme of PANI-EB is also shown at the top of the figure; the main peaks assigned to 1 s $\rightarrow$ π^* transitions are also indicated. Deconvolution of the experimental N K XANES spectrum was done using the (SPSS, 1995) with Voigt bands (Voigt area mode with varying widths) and linear baseline (linear, D2 mode). N K XANES spectrum was obtained in a spherical grating Monochromator (SGM) beam line (dipole magnetic field of 1.65 T and critical energy of 2.08 keV) at the Brazilian National Synchrotron Light Laboratory (LNLS, electron energy of the storage ring of 1.37 GeV). This line can operate in the energy range from 250 eV to 1000 eV, which covers the K edges of carbon (277 eV), nitrogen (392.4 eV), and oxygen (524.9 eV). The SGM beam line has a focused beam of roughly a 0.5 mm^2 spot size with spectral resolution E/ΔE better than 3.000 and the spectra were recorded in the total electron yield (TEY) with the sample compartment pressure of 10^{-6} Pa. The TEY detection can be briefly described as follows: I(replacement current of electrons) $\propto$ I(emitted electrons) $\propto$ I(absorbed electrons).

samples). For instance, in **Figure 3** is schematically represented the absorption of an N K shell electrons (1 s level) of an atom bonded in a solid material. The absorption occurs if the incident photon energy is transferred to an electron strongly bounded to the atom with sudden changes in the absorption coefficient. The X-ray absorption spectra can be also used for analytical purposes, because the energy edges are characteristic of each chemical element [48–50].

Our group has been used X-ray spectroscopy to investigated different conjugated systems, [16, 17, 23, 25] such as polymers and dyes and their nanocomposites with clays and other materials. The N K-edge XANES spectrum of PANI in its emeraldine base form (EB) is dominated by 1 s $\rightarrow$ π^* transitions whose energy values and intensities are related to the oxidation and doping states of PANI (see **Figure 3**). The use of multiple edges permit to probe the polymer or the clay structures such as in the case of polymer-clay nanocomposites.

2. Example of recent investigated system

2.1 Polyaniline-clay materials under heating

Our group have been studied conducting polymer-clay nanocomposites a more than a decade; the main reason is to correlate the electrical and thermal properties

of the material with the structural backbone and molecular arrangements of the interlayer polymer. The bulk properties of a conjugated polymer is correlated to the arrangement of its chains [51–53]. By intercalation into clays, it is possible to increase the polymer properties by changing its molecular arranging, but there is also an improvement of properties by interaction with the clay layers. The all reasons for the polymer-clay synergism is not yet completely understood, however many data was acquired in the literature for many polymer layered materials [54–56]. Nanocomposites formed with inorganic host structures and polyaniline and its derivatives have been one of the most studied systems. Among the inorganic hosts employed to confine conducting polymers, clays are frequently used. Our group, have been dedicate much effort to study such system by using mainly resonance Raman and X-ray spectroscopies as the main technique.

Our studies of the structure of PANI intercalated into MMT layers obtained by polymerization in aqueous suspension has modified-JGB-like units (*m*-JGB) in its backbone (see **Figure 4**) [15, 16, 24]. This result was very important in the literature because clearly shown that only using more conventional techniques, such as FTIR and EPR, is not possible to infer conclusively the exact nature of the PANI structure. In addition, our resonance Raman and X-ray absorption studies showed that intercalated PANI has a different chemical backbone than the conventional polymer (free PANI in its emeraldine salt state). More recently, we are interested to investigate the changes of the molecular structure of intercalated anilinium into montmorillonite clay (An^+-MMT) during heating treatment. **Figure 5** shows the resonance Raman spectra of An^+-MMT (see ref. [15, 16] for the description of synthesis of An^+-MMT) under heating at 100°C as a function of time. It is possible to see that the relative intensities of bands related to polaronic units of PANI at ca. 1180 and 1340 cm^{-1}, and also the bands related to cross-linked phenazinic segments at 580, 1380, and 1645 cm^{-1} increase as the time under heating also increases. These changes can be associated to the polymerization of intercalated An^+ without the use of external oxidant, like ammonium persulfate. After one day, there is no more changing.
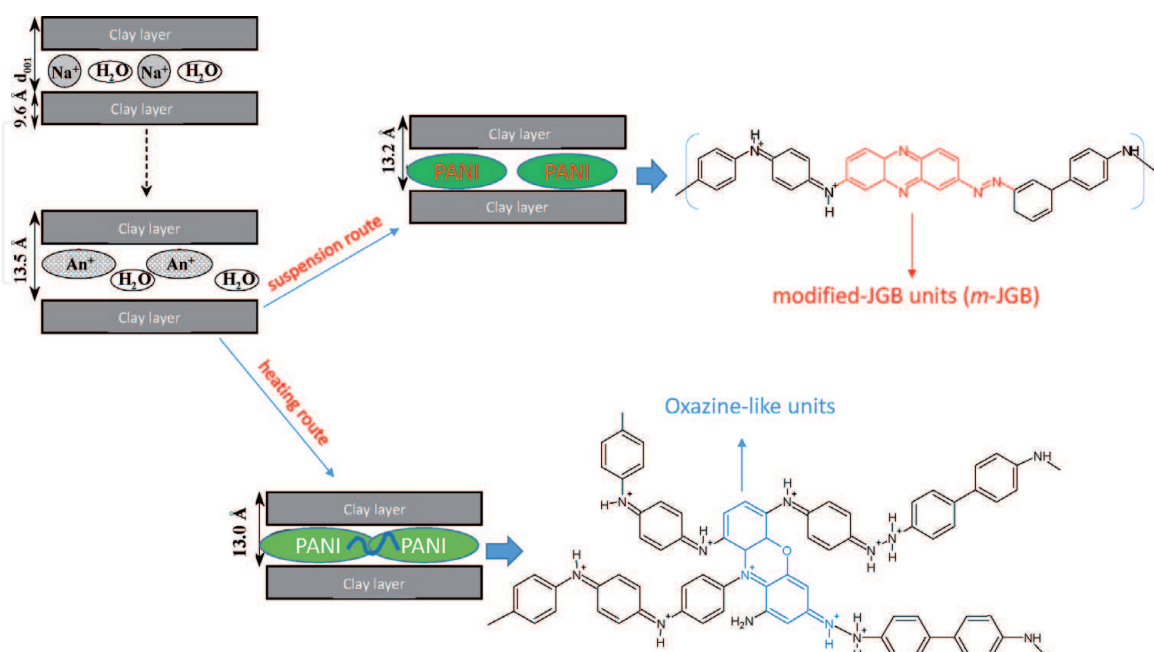

Figure 4.
Schematic representation of intercalation of anilinium (an^+) ion into MMT clay layers and their following polymerization in two different routes. XRD patterns and d_{001} values of powdered samples were obtained on a Rigaku diffractometer model Miniflex using Cu Kα radiation (1.541 Å, 30 kV, 15 mA, step of 0.05°). The possible molecular structures of intercalated PANIs are also displayed.
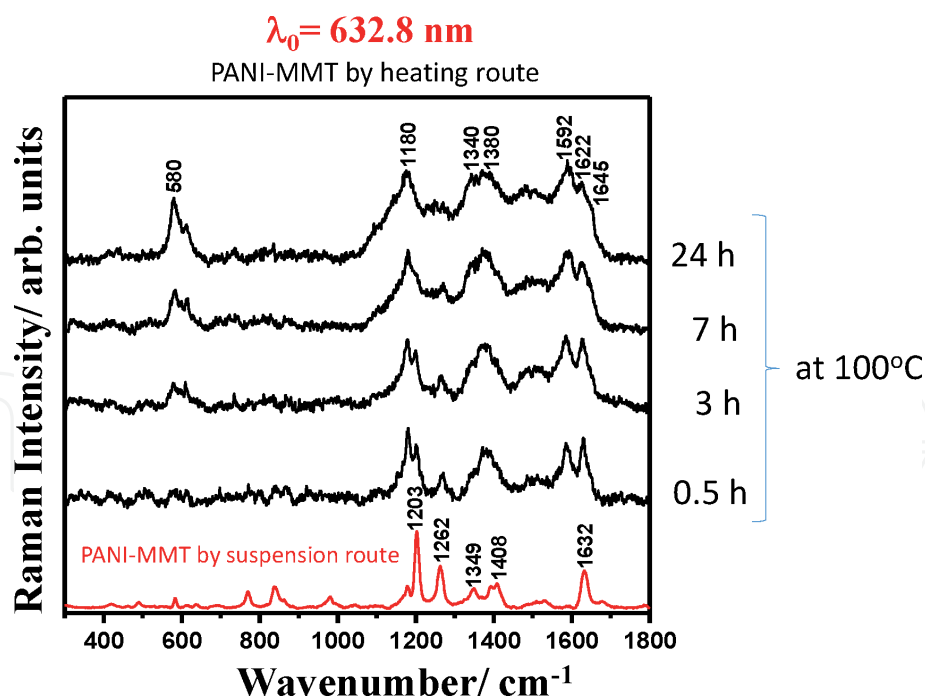
Figure 5.
Resonance Raman spectra of PANI-MMT nanocomposite obtained by suspension route and the an⁺-MMT material under different times (indicated in the figure) of heating at 100°C in air inside an oven. All experiment was done at 100°C. the spectra were acquired in a Renishaw Raman system 3000 equipped with a CCD detector and an Olympus microscope. The laser beam was focused on sample by a 50x lens. Laser power was always kept below 0.7 mW at the sample in order to avoid laser-induced sample degradation. The experiments were performed under ambient conditions using a back-scattering geometry. The samples were irradiated with 632.8 nm ($E_0 = 1.96\,eV$) line of a He–Ne laser.

Hence, it must to emphasize that the RR spectrum of PANI-MMT prepared by heating treatment (spectrum at 24 h) is completely different to the PANI-MMT prepared by *in situ* polymerization in aqueous suspension (spectrum in red). The characteristics bands related to Janus green-like (JGB) units (1203, 1408, and 1632 cm^{-1}) are not observed in the spectrum of PANI-MMT prepared by heating. Hence, the possibility to obtain a PANI only by heating is also very important, however the results clearly show that the polymer obtained in this route is also different from the PANI-MMT obtained from suspension route (see **Figure 4**). This new result clearly demonstrated the great potential of the resonance Raman to the elucidation of structures of intercalated polymers into clay nanocomposites.

We also have recently studied the thermal effects over the structure of PANI-MMT nanocomposites. **Figure 6** shows the resonance Raman spectra of PANI-MMT nanocomposites obtained by suspension route and submitted to heating process in air atmosphere at indicated temperatures. The samples were irradiated with 632.8 nm (E$_0$ = 1.96 eV) and 488.0 nm (E$_0$ = 2.54 eV) laser lines. The first thing to be considered is that PANI-MMT nanocomposites showed signal up to 300°C (similar behavior was observed for *in situ* Raman measurements during heating [24]).

The bands related to the *m*-JGB (see **Figure 4** and Raman spectra at 632.8 nm in **Figure 6**) groups are seen up to 200°C, at higher temperatures the bands at 1201, 1412 and 1630 cm^{-1} (related to the *m*-JGB segments) decrease, but at the same time, the bands at 574, 1401, and 1620 cm^{-1} assigned to Oxazine-like units (cross-linking segments, see **Figure 4**) increase. At 488.0 nm, a similar behavior is observed; however only the band at 1401 cm^{-1} associated to Oxazine-like units is clearly seen. This behavior can be rationalized considering that *m*-JGB units are degraded at higher temperatures and the cross-linked PANI-ES bands prevails, it shows that the intercalated polymer has higher thermal resistance than observed in free PANI-ES and PANI-MMT composites.
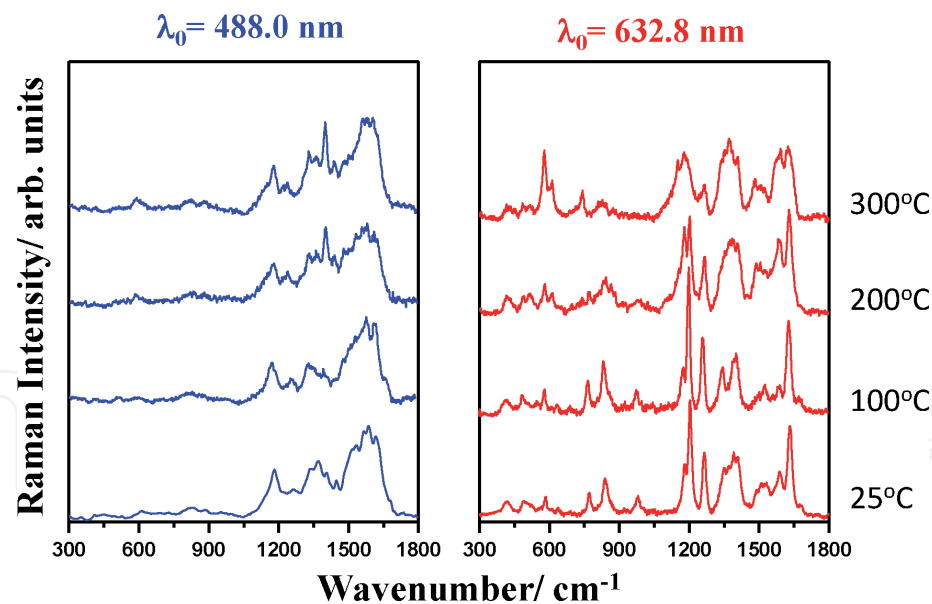
Figure 6.
Resonance Raman spectra of PANI-MMT nanocomposite obtained by suspension route and submitted of heating at indicated temperature in air inside an oven. The spectra were acquired in a Renishaw Raman system 3000 equipped with a CCD detector and an Olympus microscope. The laser beam was focused on sample by a 50x lens. Laser power was always kept below 0.7 mW at the sample in order to avoid laser-induced sample degradation. The experiments were performed under ambient conditions using a back-scattering geometry. The samples were irradiated with 632.8 nm ($E_0 = 1.96\,eV$) line of a He–Ne laser and 488.0 nm ($E_0 = 2.54\,eV$) line of an Ar⁺ laser.
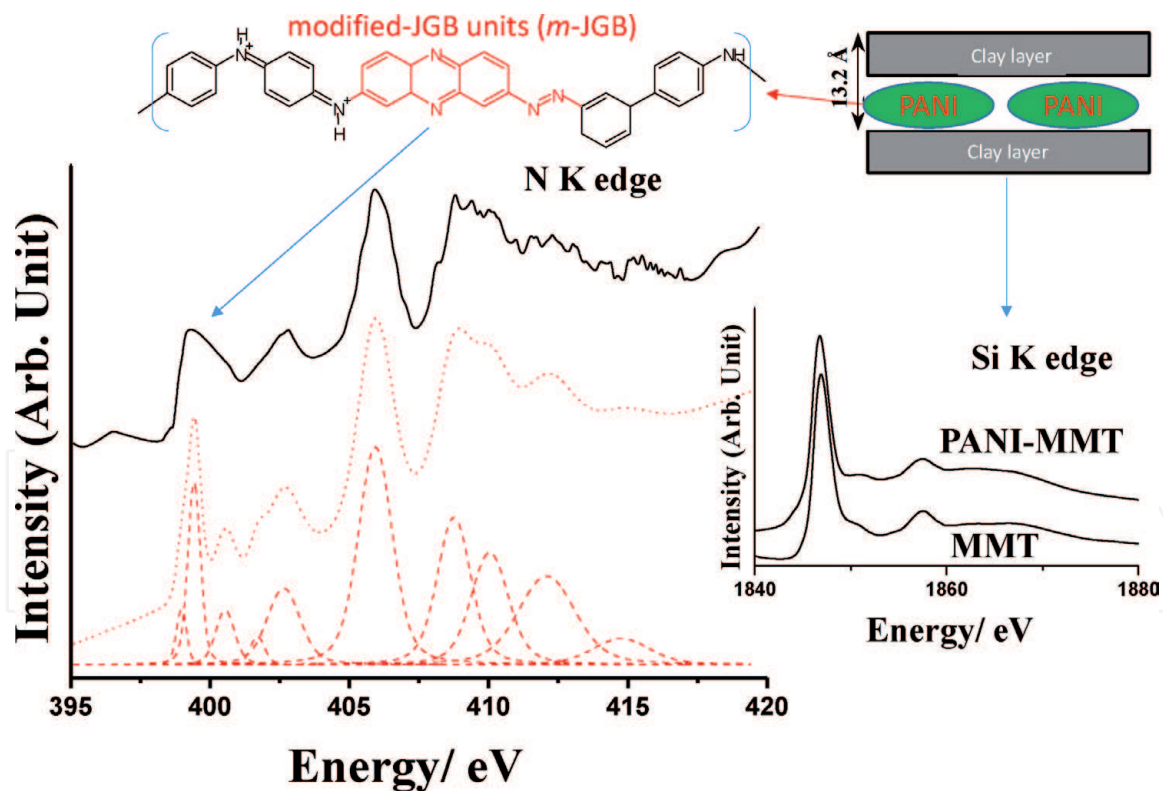

Figure 7.
N K XANES spectra of powered samples of PANI-MMT nanocomposites. The black top continuous line represents experimental spectra. The Voigt bands used in the deconvolution of the experimental spectrum are shown below the experimental data (red dashed lines, − − −). The sum spectrum of the Voigt bands is also displayed (red pointed line, ···). The Si K XANES spectra of powered samples of MMT and PANI-MMT are also shown inside the figure. Silicon K-edge spectra were recorded using the total electron yield detection and the samples chamber at ca. 10^{-6} Pa. All energy values in the Si K-edge spectra were calibrated using the first resonant peak in the Si K XANES spectra for monocrystalline silicon.

The X-ray absorption studies permit the study of polymer and clay at same time just by selection of appropriate photon energy to probe a specific atomic edge.

Our group have been studied a lot of nitrogen and silicon contend compounds in order to understand to the influence of the chemical structures and its environments over the atomic edges values (mainly Nitrogen, Carbon and Silicon). For instance, **Figure 7** shows the XANES spectra at N and Si K edges of the PANI-MMT nanocomposites. The N K edge gives many peaks related to the complex conjugated structure of the PANI. However, at Si K edge the spectra are simpler due to the regularity of silicon sites into clay layers and by the small influence of intercalated polymer over the electronic properties of clays.

3. Conclusion and future remarks

The screening of the electronic and vibrational structure of polymer-clay nanocomposite through resonance Raman and X-ray absorption spectroscopies has been decisive in determination of their structure and in the study of the interactions between the clays and intercalated polymers in a myriad of synthetic conditions. In fact, by selecting the appropriate photon energies it is possible to study in particular the specific segment of the polymer or clay. The new Raman instruments and new synchrotron rings can give better spectroscopic data associated to a very higher spatial resolution. This open the possibility to study localized inhomogeneity, specific chemical modifications and many other aspects of these extraordinary materials derived from clays.

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