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Introductory Chapter: Polymers and Clays - A Fruitful Combination

Gustavo Morari do Nascimento

1. Introduction

1.1 Clays and clay materials

The synthesis and study of materials based on clays and/or clay minerals with polymers are one of the widest fields of research in materials science and technology. Characterization followed by application of many derived clay materials is a big deal in clay science and technology. **Figure 1A** shows that in 2021, more than 16,000 papers having "clay" and "polymer" as keywords were published since 1998. In addition, **Figure 1B** shows that a group of conducting polymers represents more or less 20% of total polymers studied in composites and/or nanocomposites with clays. In addition, **Figure 2** displays that at least 15 different research fields mainly concentrated on chemistry and polymer sciences, environmental sciences, materials and nanotechnology. These two graphs clearly show that polymer clay-derived materials are one of the focuses in the science of advanced materials. Our group has been dedicated to the preparation and characterization of materials consisting of conducting polymers from polyaniline family with clays [1–11]. Among the different techniques used for structural investigation, resonance Raman spectroscopy and Synchrotron X-ray techniques are the most important for these systems.

The term "clay" was defined as "...a naturally occurring material composed primarily of fine-grained minerals (< 4μm), which is generally plastic at appropriate water contents and will harden with dried or fired" [12–15]. Likewise, the term "clay mineral" can be defined as "...phyllosilicate minerals and minerals which impart plasticity to clay and which harden upon drying or firing." Since the origin of the mineral is not part of the definition, clay mineral (unlike clay) may be synthetic. Hence, analyzing the fine-grained clay particles in detail is only possible by a combination of advanced spectroscopic and microscopic techniques [16]. Clays are aluminosilicates where the aluminum can be replaced by magnesium and iron atoms, resulting in an excess of negative charge that is balanced by alkaline or alkaline earth elements. Each clay has different composition, dehydration properties, structural failure limits, decomposition products, cation exchange capacity (CEC), and other useful properties and economic interests.

Clays layers are formed by tetrahedral (T) and octahedral (O) sheets bonded by oxygen atoms. Unshared oxygen atoms are present in hydroxyl form. Two main arrangements of T and O layers are observed: (1: 1) and (2: 1) (T:O) clays. The (1: 1) group is known as kaolin group, with the general composition of $Al_2Si_2O_5(OH)_5$ and the layer thickness of ~0.7 nm [12–14, 17]. In addition, the second main arrangement (2: 1) is well known as phyllosilicates, where one octahedral sheet is sandwiched between two tetrahedral sheets (2:1) with a total thickness of 0.94 nm. When silicon
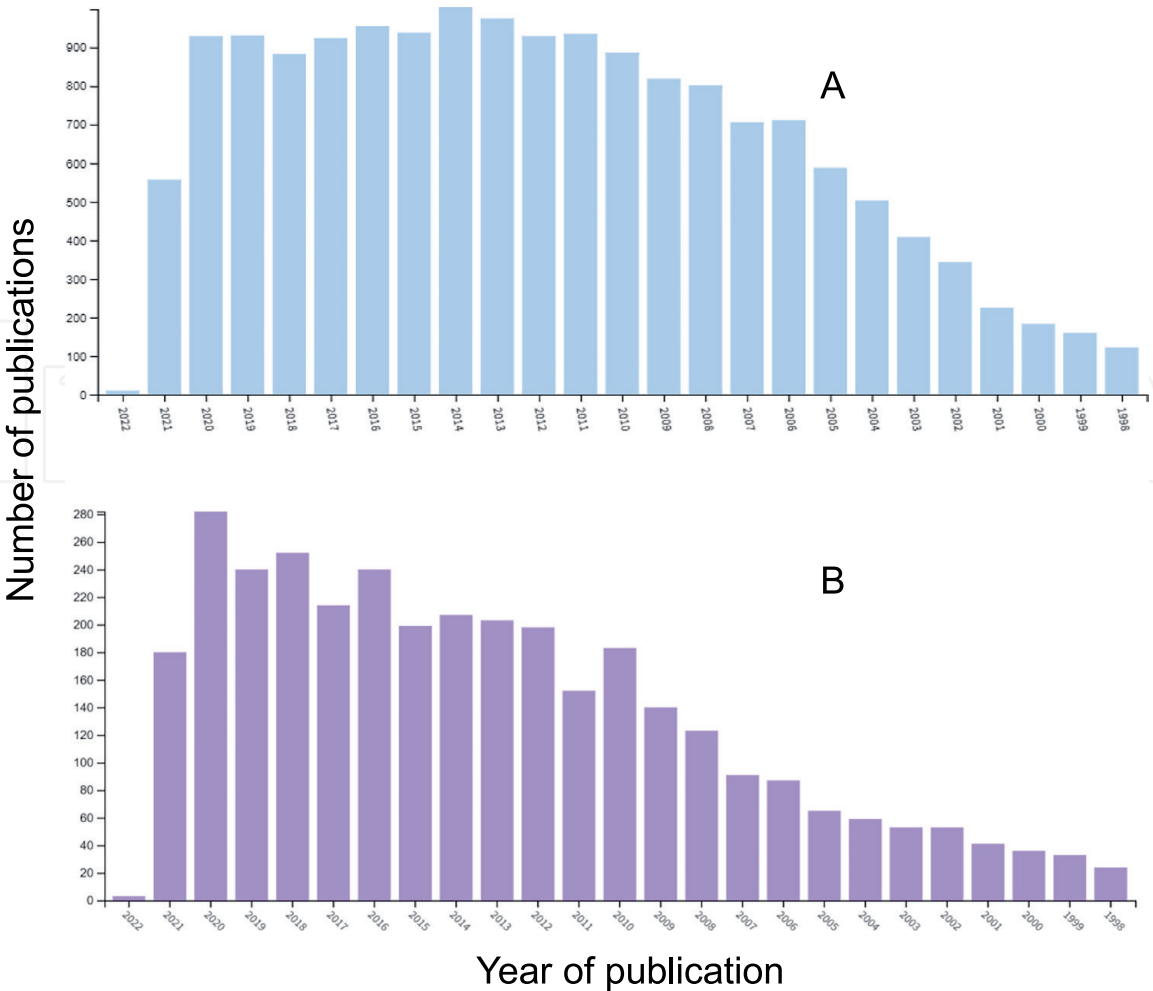
Figure 1.
Number of publications by year for the keywords: A—"clay*" and "polymer*" and B—"clay*" and "polymer*" and "conducting*" in the text. The research was done on October 10, 2021, using the web of science database. The total score found are 16.861 and 3.480 papers for graphs a and B, respectively.
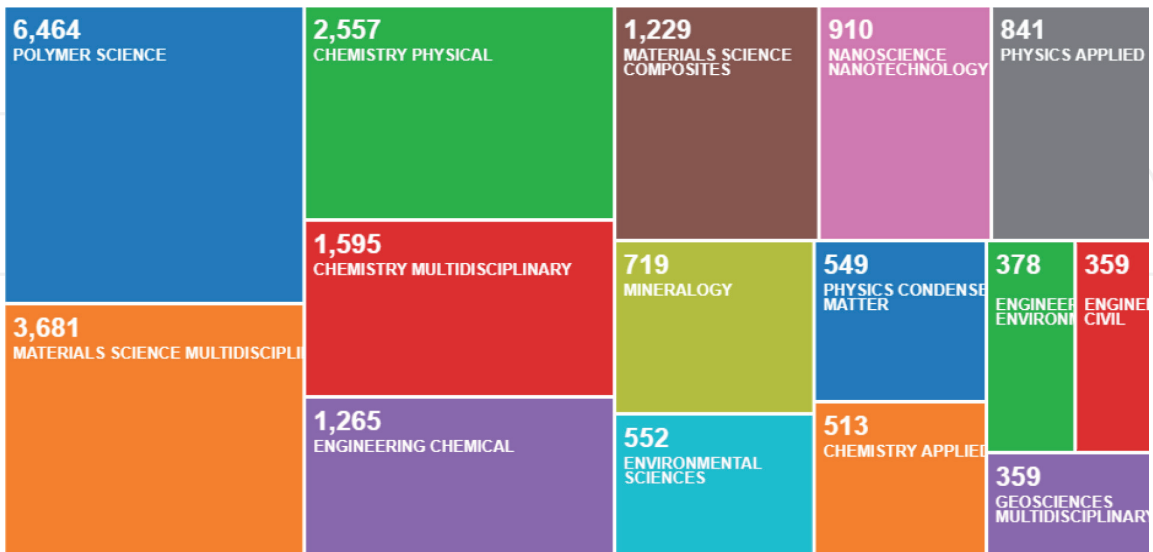
Figure 2.
Number of publications by year having the keywords "clay*" and "polymer*" in the text divided by the main research areas or categories. The research was done on October 10, 2021, using the web of science database.

in tetrahedral sheets is substituted by aluminum, the 2:1 structure is called mica. The negative charge generated by this change is equilibrated by the presence of potassium cations between the layers. Because of the equal size of K^+ cation and the hole

created by Si/Al tetrahedral sheets, there is no inter-layer spacing. Hence, no swelling or exfoliation of 2:1 layers is possible. When the aluminum cations in the octahedral sheets are partially substituted by Mg^{2+} or Fe^{2+} cations, the smectite clay group is formed, whose structure consists of a central sheet containing octahedral groups $(MO_4(OH)_2)$ bonding to two tetrahedral layers (MO_4) producing layers designated T:O:T [17] (see **Figure 3**). Ions of aluminum, iron and magnesium occupy the octahedral sites, while the centers have tetrahedrons of silicon and aluminum ions.

The T:O:T layers assume a parallel orientation, and the negative electric charge is neutralized by the presence of hydrated positive ions that are in the interlayer region [17]. These clays have high-surface adsorption capacity and catalytic activity in organic reactions. The montmorillonite (MMT) is the most common smectite clay, and the negative charges of the layer arise mainly from substitution of aluminum by magnesium ions in octahedral sites. In addition, the swelling properties, and thermal, chemical and colloidal dispersion stabilities probably are responsible for the extensive use of the MMT clay (ca. 50%) in the polymer clay-derived materials. In this introductory chapter, we will give en passant about the main points about polymers and clays —a fruitful combination.

1.2 Polymer clay materials

A polymer clay material is made by a physical and/or chemical combination of a polymer and synthetic or natural clay. The clay platelets can improve the mechanical, thermal, gas and fire barrier retardancy properties of the polymer. The improvements depend strongly on mechanical and physical dimensions of the clay, the interfacial adhesion between polymer and clay and especially on the aspect ratio of the clay. The aspect ratio of the clay is very important and crucial for many properties in composites, such as electrical, mechanical and thermal properties [18, 19].

Polymer nanocomposite is defined as a composite material in which at least one dimension of at least one component is in the nanometer size scale (< 100 nm) [20]. In recent years, the nanocomposite research area has created efficient and powerful
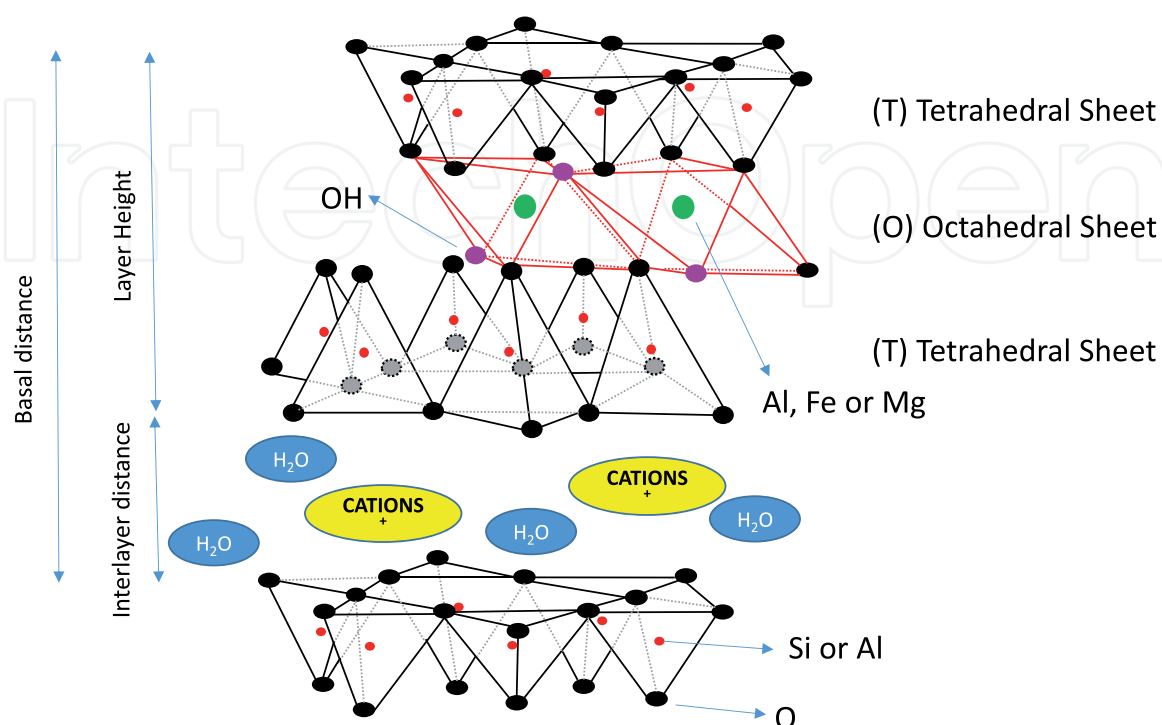
Figure 3.
Schematic representation of montmorillonite clay (MMT).

strategies to upgrade the structural and functional properties of natural and synthetic polymers. Polymer nanocomposites have generated great attention because of superior properties such as strength, toughness and fire resistance far from those of regular micro-composites and comparable with those of metals. The existence of one nanoscale phase tremendously increases the interfacial contact between the polymer and clay. As a consequence, the improvement of the polymer properties, such as mechanical, thermal barrier and flame retardancy, durability and chemical stability, scratch/wear resistance and biodegradability, as well as optical, magnetical and electrical properties, has been observed [21–24]. Recent investigations using continuum mechanics modeling show that the enhancement of nanocomposites properties is highly dependent on the peculiar features of nanofiller material, in particular, its content, aspect ratio and the ratio of filler mechanical properties to those of the matrix [25].

Polymer clay nanocomposites can be made by direct mixture of two aqueous solutions containing the monomer and the clay suspension, respectively (see **Figure 4**), followed by polymerization induced by thermal or light sources or by adding chemical oxidants [26, 27]. Afterward, if the major part of the polymer is produced outside the interlayer space, the resulting compound is named as *Ex situ* nanocomposite. The initial clay concentration can be changed in an aqueous solution in order to completely exfoliate the layers. Hence, the resulting material is known as exfoliated polymer clay nanocomposite. In another route, the monomer is previously intercalated in the interlayer space before the polymerization procedure. Then, the resulting material is known as *in situ* nanocomposite because the major part of the polymeric content is inside the clay interspace (see **Figure 4**). The polymer clay hybrids started with the synthesis of nylon-6-clay hybrid (NCH) produced in 1986 under Toyota Central Research and Development Laboratories. Then, the same strategy was employed in the formation of polymer clay hybrids with various polymeric systems, including epoxies, polyesters, polyimides, nitrile rubber, polypropylene, polyurethanes, polystyrene and
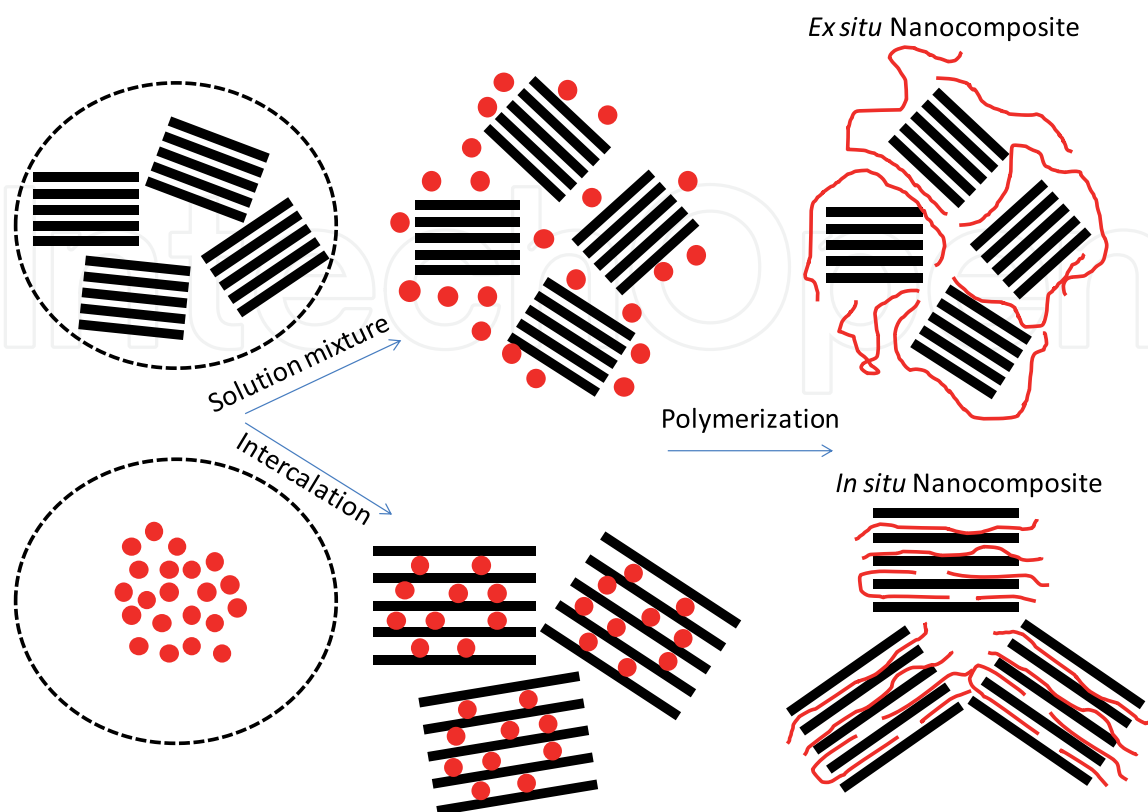
Figure 4.
Schematic representation of two types of preparation of polymer clay nanocomposites.

polysiloxanes. Traditionally, the clay layers must be previously treated with an organic agent to ensure good dispersion of clay layers within the polymer matrix. It is very hard to mix clay layers in most polymer matrices because of their high face-to-face stacking and intrinsic hydrophilic character. These characteristics make most clays incompatible with hydrophobic polymers, and only a few hydrophilic polymers such as poly(ethylene oxide) and poly(vinyl alcohol) can be miscible with clay layers [28]. Modification of clay layers with hydrophobic agents is necessary in order to make clay more compatible with polymers and preclude formation of non-mixed phases.

1.3 Conducting polymer-clay materials

Among the polymers used for production of polymer clay materials are the intrinsically conducting polymers (ICPs). These classes of polymers are conjugated polymers that can be doped by chemical, electrochemical or photochemical processes with an increase of their conductivities (see **Figure 5**). The doping is reversible, and the polymer can return to its original state without major changes in its structure [29–34]. In the doped state, the presence of counter ions stabilizes the doped state. All conductive polymers (and their derivatives), for example, poly(aniline), poly(pyrrole), poly(thiophene)s, poly(p-phenylene-vinylene)s, poly(heteroaromatic vinylene) (f, where Y = NH, NR, S, O), among others (see **Figure 5**), may be doped by p (oxidation) or n (reduction) process. Our group has been synthesizing polymer clay nanocomposites formed by poly(aniline) (PANI, see **Figure 6**) and its derivatives with MMT clay for almost two decades [1–11].

The adsorption of aromatic compounds such as aniline on MMT clay was investigated a long time ago, and the clay property to generate colored species by
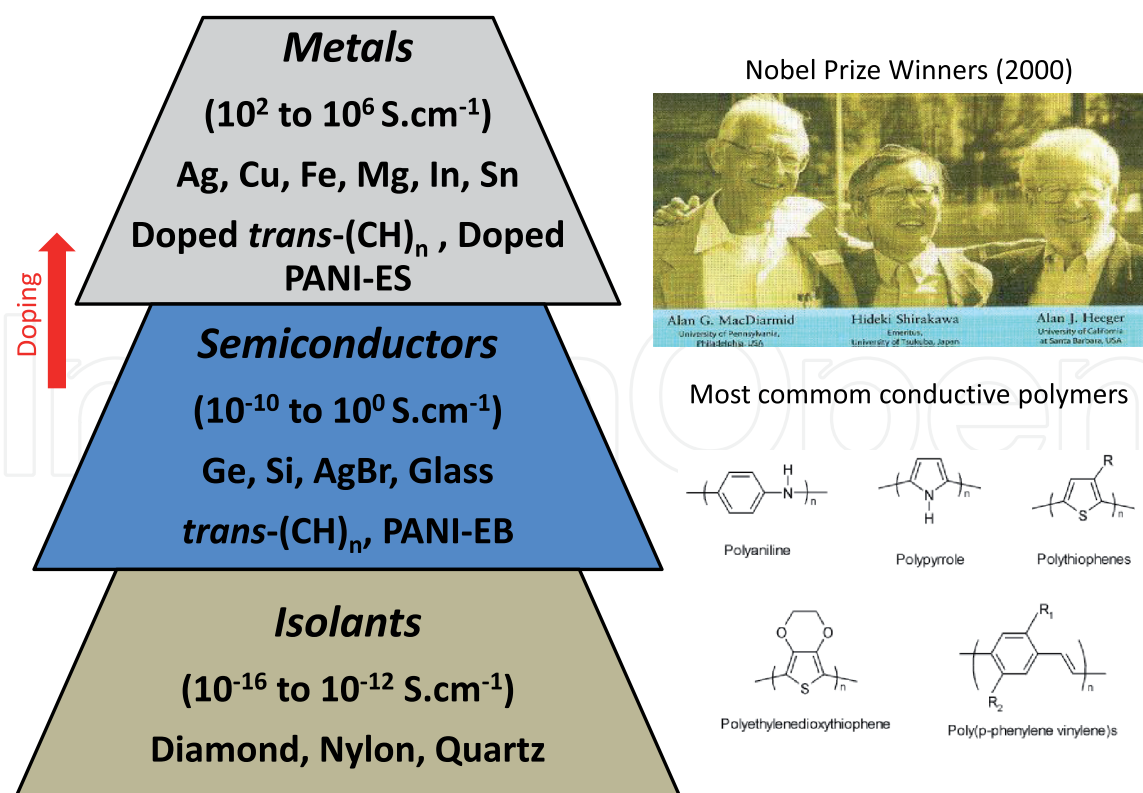
Figure 5.
The Nobel winners in chemistry (Hideki Shirakawa, Alan J. Heeger, and Alan G. MacDiarmid [29–31]) for the discovery and development of conducting polymers and the chemical structures of the most investigated conductive polymers. In addition, the conductivity values for different materials are also displayed in comparison with conducting polymers before and after the doping. The doping produces (the addition of nonstoichiometric chemical species in quantities low ≤10%) dramatic changes in the electronic, optical, electrical, magnetical and structural properties of the polymer.
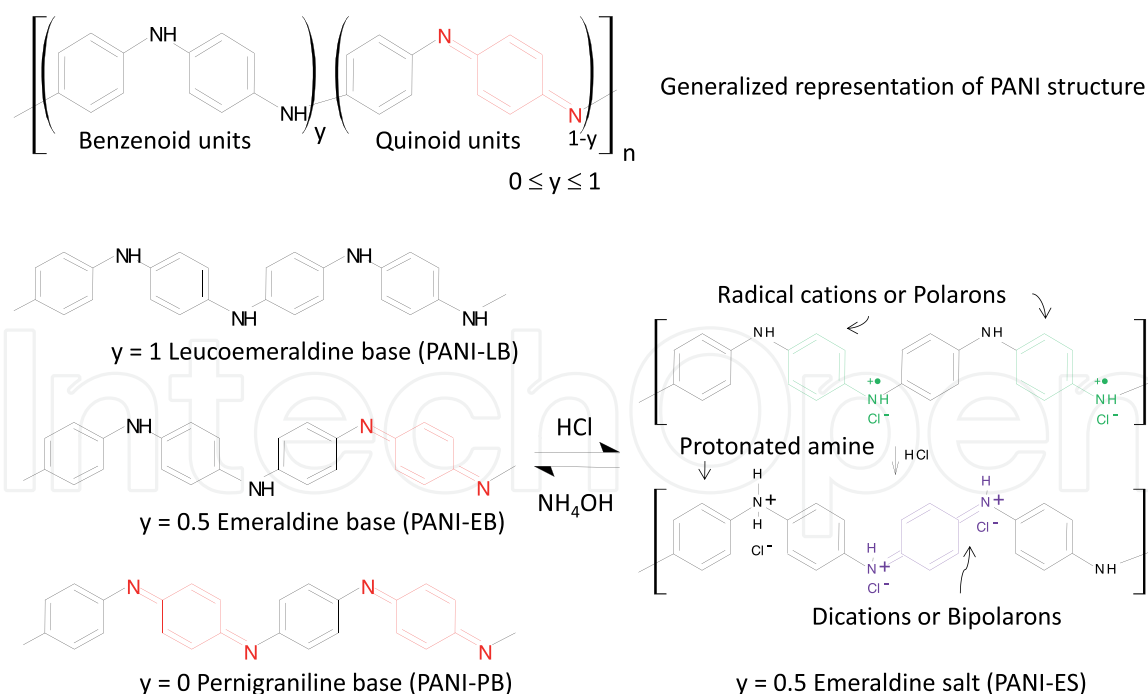
Figure 6.
Representation of PANI structure and its most representative forms.

the adsorption of aromatic amines was on the first experimental observation. The well-known behavior is the blue color generated by the adsorption of benzidine (4,4′-diaminobiphenyl) into clay layers. First, investigations reported that films of MMT containing metal ions become black after immersion in aniline, suggesting the polymerization of the monomer [35–39]. By using resonance Raman spectroscopy (RR), Soma and Soma [40–44] discovered that the adsorption of liquid aniline on Cu^{2+} or Fe^{3+}-MMT causes the formation of the polymer. Soma and Soma suggested that the polymeric structure is equal to that generated electrochemically but with the presence of azo bonds (-N=N-). Another important observation is that intercalated PANI showed FTIR bands at 1568, 1505, 1311 and 1246 cm^{-1} characteristic of the conducting emeraldine state, but they were shifted to higher frequencies to the spectrum of free polymer. According to the authors, this displacement is a consequence of geometric restrictions imposed over the aromatic rings. The intercalation was confirmed by changes in the interlayer distance from 1.47 to 0.36 nm after the polymerization of aniline. Absorption bands were observed at 420 and 800 nm in the UV–vis–NIR spectrum of the material, which are the characteristic of conducting PANI form [45].

In fact, many authors prepared PANI-MMT using ammonium persulphate as an oxidizing agent, and for these authors the electronic spectra and FTIR bands were enough to characterize the PANI in its conductive state (emeraldine salt) [45–55]. However, when our group started to study this material by using resonance Raman spectroscopy (like Soma and Soma one decade earlier [40–44]) together with X-ray absorption techniques, it was revealed that the structure of intercalated PANI into MMT layers is much more complex and different from the free PANI [1–11]. The early stages of the polymerization of intercalated anilinium ions were monitored by *in situ* resonance Raman measurements. It was observed the bands of radical cation of PANI-ES (at 1167, 1318/1339 and 1625 cm^{-1}) and dication (at 1481 and 1582 cm^{-1}) and also bands due to benzidine dication at 1211, 1370, 1455, and 1608 cm^{-1}, confirming that into clay galleries, occur the head-to-tail and also tail-to-tail coupling between the aniline monomers. In the final stages of polymerization, mainly by the resonance Raman data obtained at 632.8 nm, it was confirmed to be a completely new spectrum, whose bands have no similitude with either the radical cation of

PANI-ES or the spectrum of benzidine dication. This result shows that another type of chromophore was formed. At this point, the use of XANES spectroscopy on nitrogen K-edge was fundamental. Through the analysis of several dyes, it was possible to build an extensive data library [11], and by comparative analysis, it was found that the structure of intercalated PANI also has phenazine rings. Combining all spectroscopic data, we have proposed that the best standard compound, having azo group bonded to phenazine- or oxazine-like rings in their structure, was the Janus Green B (JGB). This dye that gives out similar vibrational and electronic signatures to those of the PANI-MMT nanocomposites can be used in the future for simulation of the electronic properties.

2. Conclusion and future remarks

We really think that the polymer clay area has much more to be investigated, but with the employment of new synthetic strategies and the use of advanced spectroscopic techniques. The accumulated experience with PANI-MMT materials revealed the importance of the use of advanced and complementary spectroscopic techniques in order to give a more realistic view of the molecular structure formed in the clay layers. The screening of the electronic and vibrational structure of PANI-MMT through resonance Raman and X-ray absorption spectroscopy has been decisive in the determination of their "real" structure and in the study of the interactions between the clay layers and polymer chains. In fact, by selecting the appropriate laser line, it is possible to study in particular each polymeric segment into polymer backbone. The new Raman instruments can give better Raman imaging of the samples and open the possibility to study inhomogeneity, chemical modifications, and many other aspects of the polymer clay materials. In addition, new Synchrotron light sources will enable us to study changes in these complex materials by *in situ* measurements, resulting in spectral and imaging data. These new data are crucial for better application design and more vast use of materials derived from polymer clays.

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