

VIBRATIONAL PROPERTIES OF POLYANILINE FUNCTIONALIZED PbI₂^{*}

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Functionalization of PbI₂ with polyaniline-emeraldine base (PANI-EB) or polyaniline-emeraldine salt (PANI-ES) is demonstrated by Raman spectroscopy. Two functionalization methods were used: electrochemical polymerization of aniline onto the PbI₂ modified Pt electrode and the mechanico-chemical reaction between PANI and PbI₂. The functionalization induces changes in the Raman spectrum of PbI₂ that consist in the appearance of new Raman lines with the peaks at 80, 144 and 170 cm⁻¹. The first line is the signature of the "stacking faults" that disrupt the stacking sequence of layers I-Pb-I atomic layers along the *c* crystalline axis by the intercalation of polymer molecules. The bands at 144 and 170 cm⁻¹ are attributed to a vibrational mode associated to the Pb-NHR''₂ (R''= C₆H₄) bond.

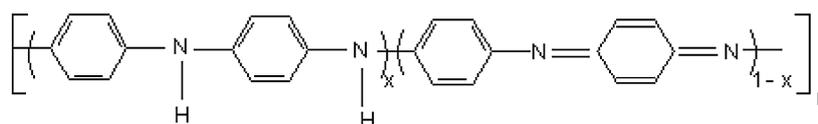
Key words: conducting polymers, PbI₂, intercalation, Raman scattering.

1. INTRODUCTION

In the last years, a special attention has been given to the basic and applicative researches of the organic/inorganic hybrid materials. Thus, detailed studies have been performed on materials as: i) isolated or conducting polymers functionalized carbon nanoparticles (carbon nanotubes, fullerene) [1], ii) composites achieved from polymers or biopolymers with different oxides (SiO₂, Al₂O₃, V₂O₅ etc. [2–4]) or metallic nanostructures (for example: poly o-phenylene diamine/Au [5], etc.), iii) inorganic semiconductors of the type CdS, CdSe, ZnS, ZnO, TiO₂ produced in the presence of polymers [see Ref. 6, 7]. For these hybrid materials have been reported different applications in the field of sensors, storage energy, biomedical and textile industry. New applications in opto-electronics are envisaged for the hybrid compounds based on the intercalated layered structures. An example presented below is the lead iodide (PbI₂) intercalated with polyaniline (PANI). In the present work, such materials

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have been prepared by: i) electrochemical polymerization of aniline on the PbI_2 modified Pt electrode and ii) mechanico-chemical route, when mechanical motions/energy-controlled chemical reactions take place between PANI and PbI_2 . PANI is a polymer whose repeating unit contains two entities with different relative weights.



Scheme 1

The reduced ($x = 1$) and oxidized ($x = 0$) form is known under the name of leucoemeraldine base (LB) and pernigraniline base (PB), respectively. The intermediate state ($x = 0.5$), in which the oxidation and reduced degrees of PANI are equal to each other is known as emeraldine base (EB). In the case of electrochemical synthesis, an often used method is cyclic voltammetry. The aqueous acidic medium frequently used is H_2SO_4 or HCl . The reaction products correspond to the doped states of PANI known as emeraldine salt (ES), leucoemeraldine salt (LS) and pernigraniline salt (PS). *A priori*, the two synthesis methods, namely electrochemical polymerization and mechanico-chemical reactions, must lead to hybrid compounds with similar properties. As layered material, PbI_2 has as rigid structurally repeated unit, an I-Pb-I layer of 0.7 nm thickness [8]. The bulk crystal is composed of atomic I-Pb-I layers arranged successively and perpendicularly along the c axis. PbI_2 features a strong intralayer chemical bonding and weak interlayer van der Waals interactions [9]. The intercalation of the PANI molecules between the crystalline I-Pb-I layers can be governed by: i) weak forces associated to physical adsorption or ii) strong forces resulting from charge transfer between the two constituents, of organic (aniline or polyaniline) and inorganic (PbI_2 crystal) nature. Using the Raman spectroscopy, we show that the formation of the PANI/ PbI_2 composite evolves in two stages. At the beginning takes place the intercalation between the I-Pb-I layers of PANI molecules by a physical adsorption process followed by the formation of a new compound resulting from the charge transfer between the two constituents.

2. EXPERIMENTAL SECTION

Slides of PbI_2 have been cleaved from a single crystal ingots of 5 cm length and 2 cm diameter, which was grown by the Bridgman method from chemically purified raw material. The crystal growth takes place by a controlled freezing

process under a temperature gradient. Because in the Bridgman-grown PbI₂ crystals the most frequently observed polytypes are 2H and 4H, the transformation of the 2H in 4H polytype was obtained by a thermal annealing at 420 K [10]. This inter-polytype transformation was monitored by the Raman line at 76 cm⁻¹, which attains its maximum for the 4H polytype.

Two routes were used to prepare the PANI/PbI₂ hybrid material. The first consists in the electrochemical polymerization of aniline (ANI) on the PbI₂ modified Pt electrode via cyclic voltammetry. For this one used a conventional three-electrode one-compartment cell, having as working electrode a PbI₂ modified Pt support and a spiral Pt wire as auxiliary electrode. The reference electrode was a saturated calomel electrode (SCE). The working electrode was immersed into aqueous solution of 0.5 M HCl or 0.5 M H₂SO₄ and 0.05 M aniline. All compounds were purchased from Aldrich-Sigma. The PANI films were obtained with a sweep rate of 25 mV s⁻¹ between -100 and +900 mV vs. SCE. In this way has been obtained PbI₂ samples intercalated with the conducting polymer of the type polyaniline – emeraldine salt (PANI-ES). Later, these samples interacted for 5 min with an aqueous 1M NH₄OH solution result in PbI₂ samples intercalated with polyaniline – emeraldine base (PANI-EB). The electrochemical polymerization of aniline on the PbI₂ modified Pt electrode has been carried out using a potentiostat/galvanostat type VOLTALAB 80 from Radiometer Analytical.

The second route consists in a mechanico-chemical reaction by which a crystalline powder of (PbI₂) mixed with 5 and 10 wt% polymer in the un-doped (PANI-EB) or doped state (PANI-ES) was compressed non-hydrostatically for ca. 2 min. at 0.58 GPa. The PANI was prepared using two solutions of: i) aniline (1.022 g, 1.09·10⁻² mol) in 25 mL of 2 M H₂SO₄ and ii) K₂Cr₂O₇ (0.56 g, 1.9·10⁻³ mol) in 25 mL of 2 M H₂SO₄, which were mixed together and left standing under ultrasonications for 2 h at 0°C. The resulting green suspension, indicating the formation of polyaniline in its emeraldine salt form, was filtered and the filter cake was washed with 1000 ml of deionized water [11]. A part was dried under vacuum at room temperature until constant mass. Another part, stirred in ammonium hydroxide solution (500 ml 1M NH₄OH) for 1 h, transforms the salt form, *i.e.*, (PANI-ES) into the base form, *i.e.*, (PANI-EB). After filtering, the oligomers were extracted with 400 ml of acetonitrile (CH₃CN) until the solvent was colorless and the remaining powder was dried as in the case of PANI-ES.

Raman studies has been carried out in a backscattering geometry with a resolution ±3 cm⁻¹ at the wavelength excitation of 1064 nm using a FT Raman Bruker RFS 100 spectrophotometer. The laser power was adjusted until 150 mW in order to prevent the samples damaging.

3. RESULTS AND DISCUSSIONS

Figs. 1a and 1b show the cyclic voltammograms of PANI deposited on the Pt alone support and PbI_2 modified Pt electrode in presence of the aqueous solution of 0.5 M H_2SO_4 and 0.5 M HCl, respectively. It is well known that cyclic voltammograms of PANI recorded in aqueous acidic media usually show two redox couples associated with inter-conversion between leucoemeraldine and emeraldine (first couple) and between emeraldine and pernigraniline (the second couple) [12]. An analyze of Fig. 1a shows that in the case of PANI electrogeneration in H_2SO_4 medium on the Pt electrode, the three oxidation maxima are situated at ca. 184, 464 and 774 mV *vs.* SCE and the corresponding reduction maxima are localized at ca. 4, 405 and 691 mV, respectively. On the

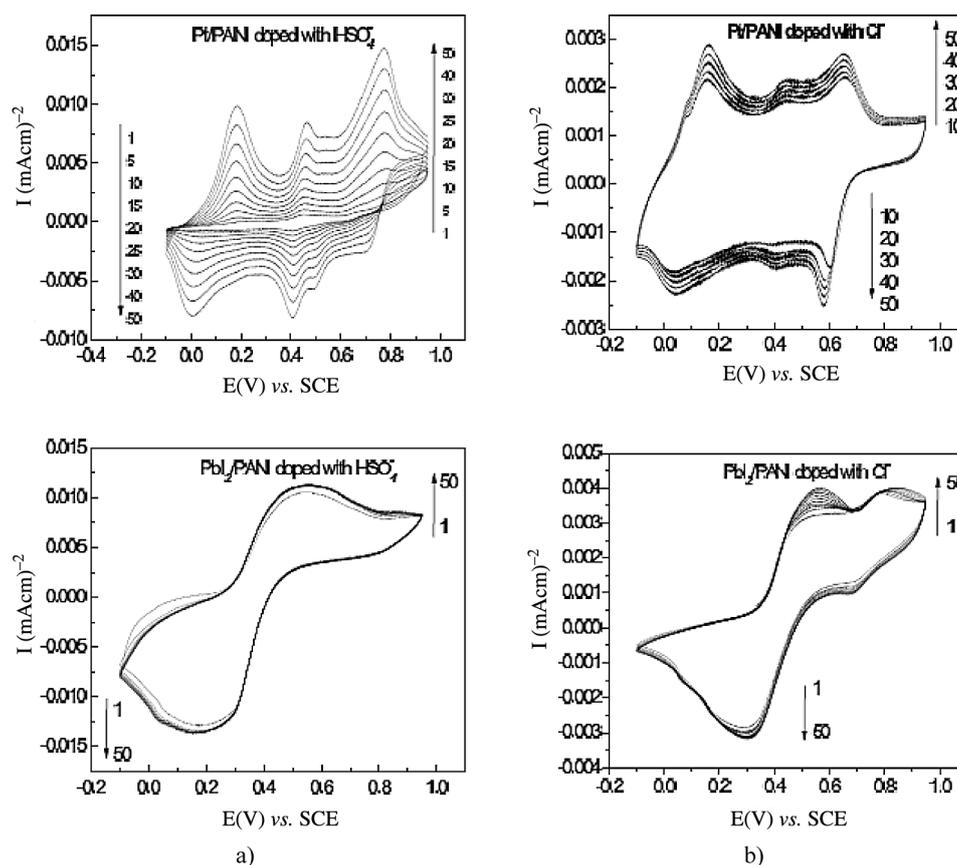


Fig. 1 – Cyclic voltammograms of the electrochemical polymerization of aniline in aqueous 0.5 M H_2SO_4 (a) and 0.5 M HCl (b) media carried out on the Pt support and PbI_2 modified Pt electrode in the potential range (-100; +900) mV *vs.* SCE with the sweep rate of 25 mVs⁻¹.

same Pt electrode, when the electrogeneration of PANI is made in an aqueous HCl solution (Fig. 1b) one observe small changes in the position of oxidation and reduction maxima; thus, the anodic maxima are situated at 161, 436 and 653 mV and cathodic peaks are localized at 37, 405 and 579 mV vs. SCE. The things are different when the electrochemical polymerization of aniline takes place on the PbI₂ modified Pt electrode. In this context, depending on the acid medium used one observe for H₂SO₄ only one redox couple with the oxidation and reduction maximum at 541 and 169 mV vs. SCE, respectively while for HCl, two redox couples appear with the oxidation maxima at 558 and 789 mV and the reduction maxima at ca. 306 and 681 mV vs. SCE.

In this stage of the investigations arises the question if from the above electrochemical process results a hybrid material of the type PbI₂/aniline or a PbI₂/PANI composite. Before, to try to answer to this question, we note that a common characteristic of voltammograms shown in Fig. 1 is the growth in intensity of the oxidation and reduction maxima with the increase of the voltammetric cycles number.

A discussion about the reversible or irreversible character of the electrochemical transformation can be done appealing to the equations:

$$\Delta E = E_{p,a} - E_{p,c} = 0.58/n \quad (1)$$

$$E_p - E_{p/2} = 0.59/n \quad (2)$$

where: ΔE is the potential of separation of the anodic and cathodic peaks, $E_{p,a}$ and $E_{p,c}$ correspond to anodic and cathodic peak potentials, respectively, $E_{p/2}$ is the half wave potential and n number of transferred electrons [13]. In the case of a reversible charge transfer involving one electron and no coupled chemical reaction, the value of ΔE and the peak width are equal to ca. 60 mV and the ratio of the cathodic to anodic peak currents $i_{pc}/i_{pa} \approx 1$. Based on this reasoning and taking into account results shown in Fig. 1 we conclude that regardless of the type of acid, when is used a PbI₂ modified Pt electrode, the oxidation-reduction reactions which have evolved in the potential range (-100; +900) mV vs. SCE have an irreversible character. This is due to the deposition of PANI-ES on the PbI₂ modified Pt electrode. This sentence is sustained by Raman spectroscopic studies performed at the wavelengths excitation at 1064 nm, Fig. 2. The curves 1 and 4 from Fig. 2 represent the Raman spectra of PbI₂ and PANI-ES. In the low wavenumbers spectral range, 50–200 cm⁻¹, PbI₂ shows a complex band composed from the Raman lines with the maxima at 75, 96, 112, 144 si 160 cm⁻¹ which are associated with the vibration modes E₂¹, A₁¹, A₁², 2E₂¹ and 2E₁¹, respectively, all belonging to the poly-type 4H-PbI₂ crystal [14]. According to the spectrum 4 from Fig. 2, the main Raman lines of PANI-ES are found in the

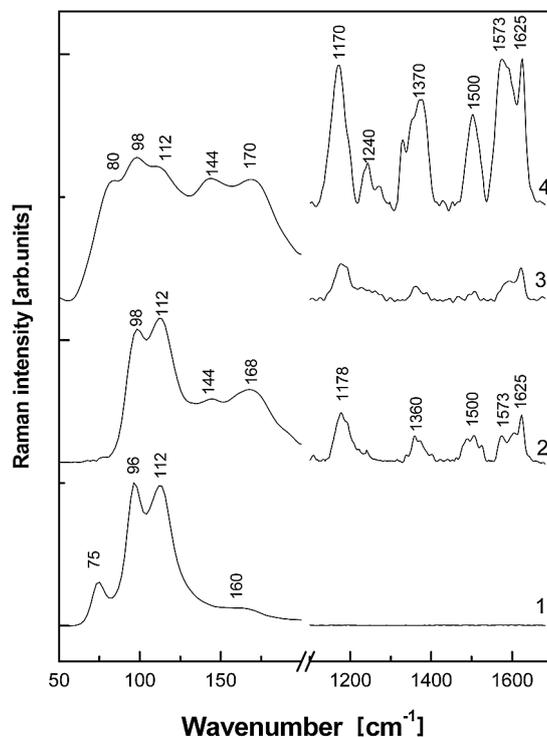


Fig. 2 – Raman spectra at $\lambda_{\text{exc}} = 1064 \text{ nm}$ recorded on the PbI_2 modified Pt electrode in the initial state (1) and after the electrochemical deposition of PANI during of 25 (2) and 50 (3) cyclic voltammograms. Spectrum 4 corresponds to the PANI-ES film deposited on the Pt support.

spectral range $1000\text{--}1650 \text{ cm}^{-1}$. The lines peaking at ca. 1170, 1240, 1330–1370, 1500, 1573 and 1625 cm^{-1} , are associated to the following vibration modes: C-H bending (B)- A_g mode, C-C stretch. (B) + ring def., semi-quinoid structure of PANI-ES, C=N stretch.+C-H bending (B), C=C stretch. (Q)+C-C stretch. (B) and C-C stretch. (B) +C-H bending (B) (B = benzene ring, Q = quinoid ring), respectively [15]. Increasing the number of cycles recorded on a PbI_2 modified Pt electrode, from 25 to 50, (spectra 2 and 3 in Fig. 2) one observe the appearance of the all specific vibrations of PANI-ES.

In the spectral range of low frequencies, $50\text{--}250 \text{ cm}^{-1}$, where are situated the Raman lines of PbI_2 , a gradual increase of the Raman lines intensity at 140 and 170 cm^{-1} appears. Thus, after the 50 cycles, the ratio between the intensities of Raman lines situated at $98\text{--}112$ and $144\text{--}170 \text{ cm}^{-1}$ changes from 10:1 to 1:1. At the first sight, the enhancement of the Raman lines at 144 and 170 cm^{-1} can be interpreted as result of an intercalation process of the PbI_2 crystal with PANI-ES. If the attribution is correct, then the same lines should be seen in the case of the intercalation with other molecules.

A good example is the case of the PbI_2 crystal intercalated with aniline. Very few studies have been dedicated to this subject. X-ray diffraction and Raman spectroscopy, by the appearance of the strong Raman lines at 996, 1030

and 1600 cm^{-1} , have confirmed the presence of aniline in the interlayer space of PbI_2 . The main conclusion of these studies was that the intercalation leads to an increase of 0.5 eV of the optical band gap [16]. New information concerning the PbI_2 /aniline interaction are obtained in this paper by Raman spectroscopy. Hybrid material lead iodide/aniline (PbI_2/ANI) has been obtained by the immersion for 24 hours of a crystalline PbI_2 sample of ca. 0.1 g in ca. 0.2 ml ANI. The Raman spectrum of the PbI_2/ANI hybrid material is presented by the curve c in Fig. 3, where one observed that the line 173 cm^{-1} is much enhanced. On the same figure are recognized the Raman lines of aniline at ca. $391, 532, 620, 815, 996\text{-}1030, 1154\text{-}1178, 1280$ and 1602 cm^{-1} which are associated with the vibration modes C-C-C out of plane bending, C-C-C in plane bending, C-C-C in plane bending, C₆-H out of plane bending, NH₂ rock.+ C-H in plane bending, C-C stretching + C-H in plane bending, C-C stretching + C-NH₂ bending and NH₂ scissoring+C-C stretching [17].

A priori, an intercalation process can be generated by a physical or chemical mechanism. In the former case, when the penetration between the atomic I-Pb-I layers is governed by a diffusion process, the layer structure is preserved so that the Raman spectrum of the final compound appears as a sum of the Raman spectra of host structure and guest molecules. The absence of new Raman lines is a proof of this mechanism. In the case of the chemical mechanism, by the interactions between the host structure and guest molecules one obtain new compounds of different morphology, crystalline structure and

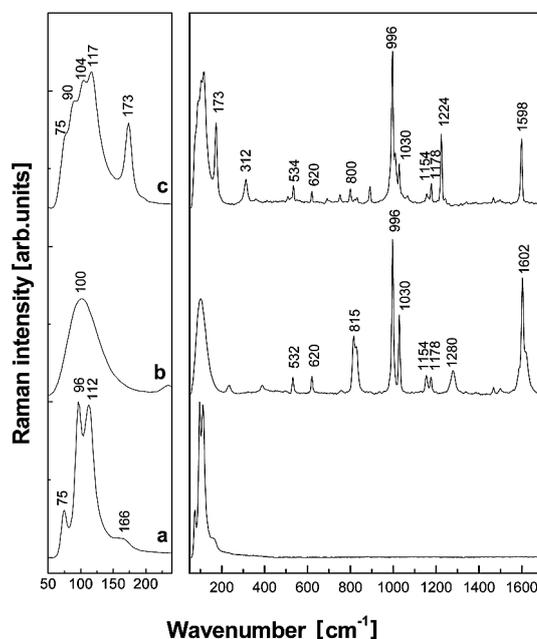


Fig. 3 – Raman spectra at $\lambda_{\text{exc}} = 1064\text{ nm}$ of: a) crystalline PbI_2 -powder, b) aniline and c) PbI_2 intercalated with aniline.

composition. Evidently, the Raman spectrum of the new compound will reveal significant modifications of the Raman spectra of the two constituents. Such a case is those of PbI_2 intercalated with aniline. In comparison with the Raman spectrum of PbI_2 for the intercalated sample a complex band covering the spectral range $50\text{--}250\text{ cm}^{-1}$ is observed which in the final stage reveals lines localized at ca. 75, 90, 104, 117 and 173 cm^{-1} . The Raman line at 96 and 112 cm^{-1} observed in the Raman spectrum of PbI_2 are shifted to 104 and 117 cm^{-1} fact that indicates a chemical interaction between PbI_2 and aniline. Penetration into PbI_2 layer structure of aniline molecules disrupts the stacking sequence continuity of I-Pb-I layers along the c axis by the formation of staking faults whose Raman signature is revealed by the line at ca. 90 cm^{-1} . Recently, similar results have been reported for the PbI_2 crystal intercalated with pyridine [18]. The appearance of the new Raman line at ca. 312 cm^{-1} has a certain significance, it may marks the formation of another material with a different morphological form. The deduction is done in the spirit of previous reported data when the PbI_2 platelets transform in another compound with the rods form [19]. Another signature of the chemical intercalation mechanism is given of the modification of Raman spectrum of guest. In this sense Fig. 3 shows a down-shift of the Raman lines of aniline from 815, 1280 and 1602 cm^{-1} to 800, 1224 and 1598 cm^{-1} and a change of the ratio between the intensities of Raman bands situated in spectral ranges $950\text{--}1000$ and $1550\text{--}1650\text{ cm}^{-1}$ from ca. $\sim 1:1$ to ca. $2:1$. The shift of the three Raman line originates in the formation of new covalent coordinative bonds of the type $\text{Pb-NH}_2\text{R}'$ where $\text{R}' = \text{C}_6\text{H}_5$. This leads to the appearance of a positive charge on the nitrogen atom of aniline which is compensate by I^- ion. The result of this interaction is the appearance of an adduct of the type $[(\text{PbI}_2)_2(\text{C}_6\text{H}_5\text{NH}_2)_4]$ fact that explains both the shifts of the Raman lines 815, 1280 and 1602 cm^{-1} and the intensities of the bands situated in the in spectral ranges $950\text{--}1000$ and $1550\text{--}1650\text{ cm}^{-1}$, the latter related of the change of masse values of the molecular oscillators. At the first sight, the association of the Raman band at 170 cm^{-1} with the presence of $\text{Pb-NH}_2\text{R}$ bond can be considered a simple logical speculation. Returning to the Fig. 2, the gradual increase in intensity of the Raman band at 170 cm^{-1} indicates that during of the electro-polymerization of aniline on the PbI_2 modified Pt electrode appear new covalent bonds of the type $\text{Pb-NHR}''_2$ ($\text{R}'' = \text{C}_6\text{H}_4$) between PANI-ES and PbI_2 . In other words a PANI-ES/ PbI_2 composite is formed. If the deduction is correct, then the 170 cm^{-1} line must be observed differently in the Raman spectra of PANI-ES/ PbI_2 and for PANI-EB/ PbI_2 compounds obtained by mechanico-chemical interaction resulted from a non-hydrostatic compression carried out at ca. 0.58 GPa for ca. 5 min. Relevant in this sense are Figs. 4 and 5.

Fig. 4 – Raman spectra of PANI-EB (a), PANI-ES (d) and the composites, obtained by mechano-chemical reaction (non-hydrostatic compression at 0.58 GPa), of the type $\text{PbI}_2/\text{PANI-EB}$ 5% (b) and $\text{PbI}_2/\text{PANI-EB}$ 10% (c).

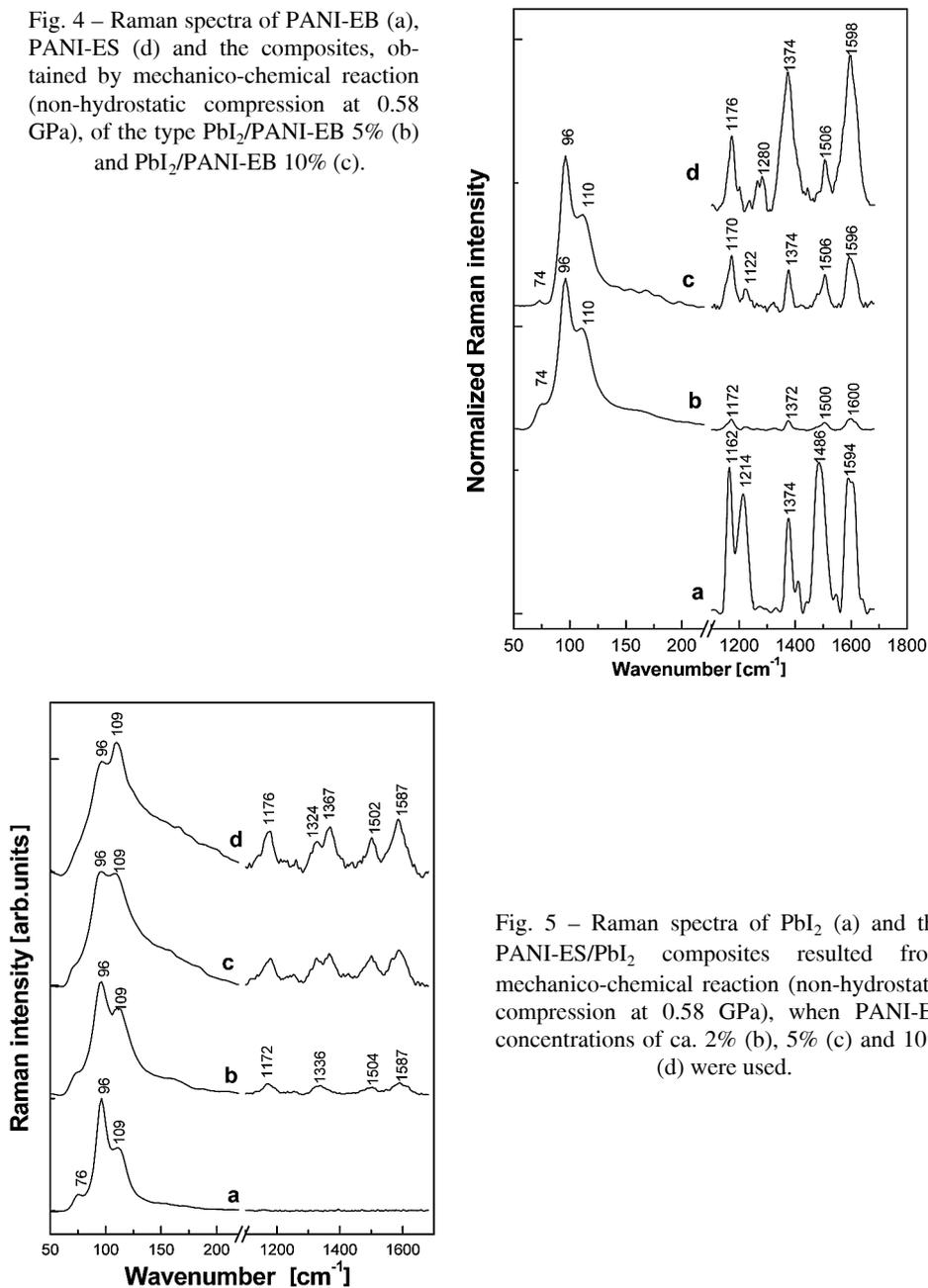
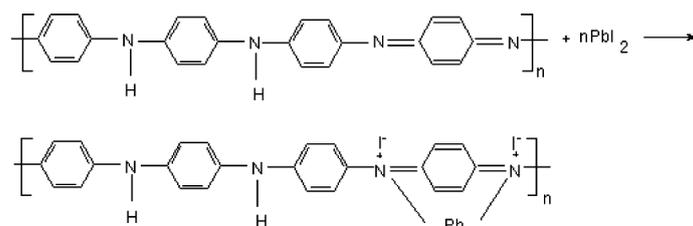


Fig. 5 – Raman spectra of PbI_2 (a) and the PANI-ES/ PbI_2 composites resulted from mechano-chemical reaction (non-hydrostatic compression at 0.58 GPa), when PANI-ES concentrations of ca. 2% (b), 5% (c) and 10% (d) were used.

Fig. 4 shows the Raman spectra of PANI-EB, PANI-ES and PbI_2 mechano-chemical intercalated with 5 and 10% PANI-EB. As for PANI-ES, the Raman spectrum of PANI-EB develops in the spectral range 1000–1650 cm^{-1} .

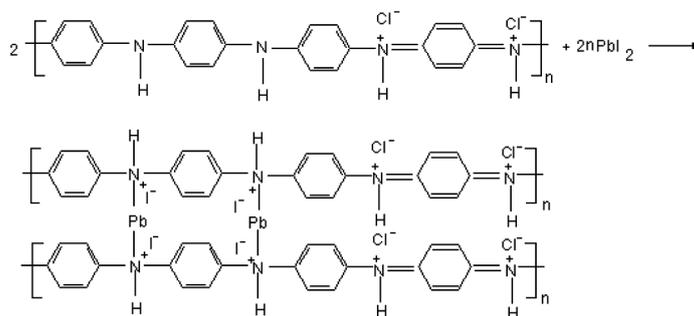
The main Raman lines of PANI-EB are situated at ca. 1162, 1214, 1374, 1486 and 1594 cm^{-1} , which according with Ref. 17 are associated with the C-H bending (Q) $-A_g$ mode, C-N stretch. + ring def. (B) + C-H bending (B), C-C stretch. (Q) + C-H bending (B), C=N stretch. + C-H bending (B) and C-C stretch. (B) + C=C stretch. (Q), vibration modes, respectively. Two facts are important to be noticed on the Fig. 4: i) the absence of the Raman line at 170 cm^{-1} indicates that in the case of PANI-EB the vibration associated to the bond $\text{Pb-NHR}''_2$ is no more present; ii) independently of the PANI-EB weight used for the mechano-chemical interaction with PbI_2 , the Raman spectra of the resulted composites (Fig. 4b and c) shown in the spectral range 1000–1650 cm^{-1} similar vibration features with those of PANI-ES.

This experimental fact must be attributed to a charge transfer between the two constituents in agreement with the below reaction:



Scheme 2

Scheme 2 shows the formation of covalent coordinative bonds $\text{Pb-NR}''_2$ which explains the appearance in Fig. 4 of the PANI-ES signature. This is illustrated by up-shift of the Raman lines 1162 and 1486 cm^{-1} to 1170 and 1506 cm^{-1} , associated with the vibration mode C-H bending (Q) and C=N stretch. + C-H bending (B), respectively. On the other side, the absence of the Raman line with maximum at 170 cm^{-1} must be correlated with the fact that the formation of new covalent coordinative bonds $\text{Pb-NHR}''_2$ as result of the



Scheme 3

addition of two macromolecular chains on the I-Pb-I layer is possible only after that PANI-EB has been transformed in totality in PANI-ES. This sentence is well supported by Fig. 5, which shows that increasing the PANI-ES weight in the polymer/PbI₂ mixture one observe a gradually growth of shoulder situated in the Raman spectral range where there is the Raman line at 170 cm⁻¹. For a better understanding of the interactions between PANI-ES and PbI₂ we propose the Scheme 3 that shows the molecular structure of the adduct noted as [(PbI₂)₂(PANI-ES)₂].

4. CONCLUSIONS

In this work are reported new results concerning the synthesis and the vibrational properties of the hybrid materials of the type PANI-ES/PbI₂ and PANI-EB/PbI₂. Our results leads to the following conclusions: i) the electrochemical polymerization of aniline on the PbI₂ modified Pt electrode as well as mechanico-chemical reaction between the PANI-ES and PbI₂ leads to the formation of a PANI-ES/PbI₂ composite based on the covalent coordinative bonds of the type Pb-NHR''₂ (R'' = C₆H₄), revealed in Raman spectrum by the line at ca. 170 cm⁻¹; ii) the mechanico-chemical interaction between PANI-EB and PbI₂ involves a charge transfer between the two constituents which confer to PANI a salt character.

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