Innovative electroluminescent nanocomposites for a new approach in polymer based light emitting devices

Scientific report

1. Preparation of electroconductive matrix

The experimental tests were carried out at this stage oriented in the direction of structural change and hence the properties of polyaniline (PANI) by the use of inorganic salts as well as to investigate the possibility of direct synthesis of polyaniline in an aqueous solution containing an electrically conductive polymer. Conductive polyaniline (doped PANI) was synthesized by a chemical method in an acid medium and in the presence of $CdCl_2$. Adding salt ions mainly has two parts: The first is doping the polymer chains, resulting in conversion of the shape of the conductive wires. The second role is to induce polymer (polymer film) specific morphology. Tests on polyaniline synthesis in the presence of polystyrene sulfonic acid (PSSA) followed both obtain a copolymer which will improve the solubility of polyaniline (PANI) in polar solvents and can deposit in thin layers by spin coating and improving the electrical conductivity of polymeric layers obtained. By suitable choice of synthesis parameters (molar ratio ANI / PSSA, temperature) were obtained water-soluble polymer solution, the electrical conductivity high enough to permit use in electroluminescent devices. The resulting products were characterized by FT-IR spectroscopy, TG / DSC / DTG, XRD, SEM.

In a first stage, experiments were directed to alter the properties of polyaniline (PANI) using $CdCl_2$. Supramolecular structure thereof may be varied depending on the nature of the ions present in the aqueous medium. Conductive polyaniline (PANI doped) was synthesized chemically in acid medium and in the presence of $CdCl_2$. Adding salt ions has two main roles. The first is doping the polymer chains, resulting in the conversion of form insulating polymer conductive form. The second role is to induce polymer (polymer film) specific morphology. The addition of other components in the conductive polymer film to obtain blends with other polymers or low molecular weight compound leads in some cases to improved film characteristics.

In the experimental studies, polyaniline was synthesized using formic acid in the presence of ammonium persulfate as the oxidant at different concentrations of CdCl2 were tested as to obtain thin films on glass substrate and poly-ethylene terephthalate (PET). Figure 1 shows a film deposited on a cylindrical substrate made of glass, in a configuration used to evaluate the electrical conductivity.

Figure 1. Modified PANI film on glass support

PSSA-PANI copolymer was obtained by the chemical synthesis of aniline in the polistren sulfonic acid medium dissolved in water using ammonium persulphate as oxidant. The polymerization reaction took place at room temperature or at 20 ° C. Aniline was added to a solution of PSSA followed by vigorously stirring for 10 minutes. ADP oxidant is added to the solution, and immediately dark green coloring of the solution is observed as a result of starting of the polymerization of aniline. Remarkably, this approach is that the required acidic environment of the

polymerization process is provided PSSA aniline dissolved in an aqueous medium whose pH is in the range necessary for optimum polymerization. In this way not only removes a reaction (the acid used for the provision of the polymerisation) yet in a PANI-PSSA graft copolymer. After completion of the polymerization, the obtained green-blue composite was purified to remove the unreacted products and oligomers. For purification, a dialysis membrane was used retaining molecular weight greater than 12,000. The dialyzed suspension (for 2 days) is dried at 60 ° C for 48 hours (Figure 2a) The obtained copolymer is soluble in a water-alcohol mixture which facilitate processing by spin coating. The resultant films are shown in Figure 2.b
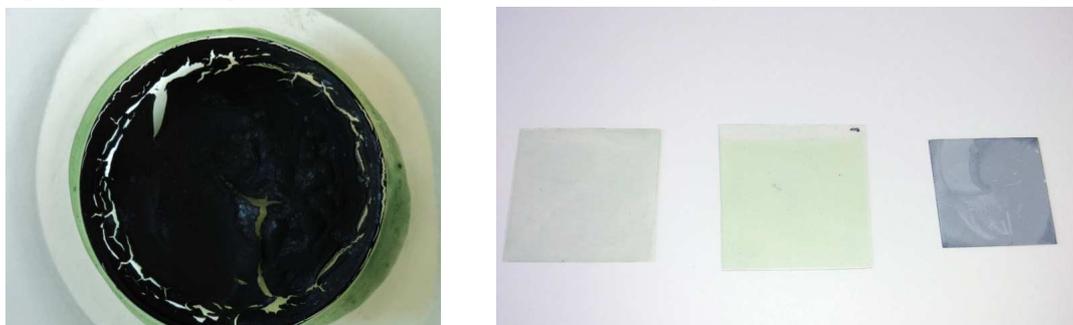
Figura 2. Copolimerul preparat PANI-PSSA: (a) După purificare și uscare, (b) Depus în strat Subțire pe suporți de sticlă și sticlă-ITO

One of the most important parameters that significantly affect the direction of redox processes involving PANI is the pH of the medium, the oxidation state of the polymer, that determine its properties. In experiments, the polymerization of aniline occurs "in situ" being removed post-processing steps, thereby preserve the basic integrity of the structure without changing the electronic and mechanical properties of the polymer.

In the experimental stage in which the polyaniline was synthesized in the presence of $CdCl_2$ the varied synthesis parameters are salt concentration introduced into the reaction and the temperature during synthesis. $CdCl_2$ concentration varied between $0.4 \div 1$ M and the temperature at which the polymerization process was carried out successively set to 0, 20 and 40 °C, observing that the crystalline phase is well developed for the sample prepared in low temperature conditions. It should be noted that the polymerization is carried out without stirring and the reaction medium is liquid, homogeneous, from the start to the end of the polymerization, irrespective of the conditions of synthesis addressed.

Regarding copolymer PANI / PSSA, we studied the influence of ANI / PSSA ratio on the morphology of the polymer film to yield homogeneous and compact structure. By varying the molar ratios of ANI / PSSA pH of the medium changes, which has an influence on the conductivity of polyaniline which is substantially improved compared to the one obtained polyaniline aqueous solution.

Fig. 3 presents the FT-IR spectra recorded for the prepared PSSA-PANI composites at three PSSA-ANI molar ratios (Figure 1c,d,e). For comparison and investigation purposes, commercially PANI-EB and PSSA were also investigated (Figure 3a,b). Oscillatory vibrations of C-H bond in benzene rings 1,4 and 1,2-disubstituted in PSSA are located at 833 and 774 cm^{-1}, respectively [18]. The wide absorption at 3436 cm^{-1} is assigned to water absorbed in the sample atribuită (sulphonic acid groups are stronly hydrophilic). From the recorded spectrum of PANI-EB (Fig. 3b) one can

observe the characterisitic peak at 1593 cm^{-1}, which is due to the C=C stretching in the quinoid ring, the 1378 cm^{-1} peak typical for C-N stretching.
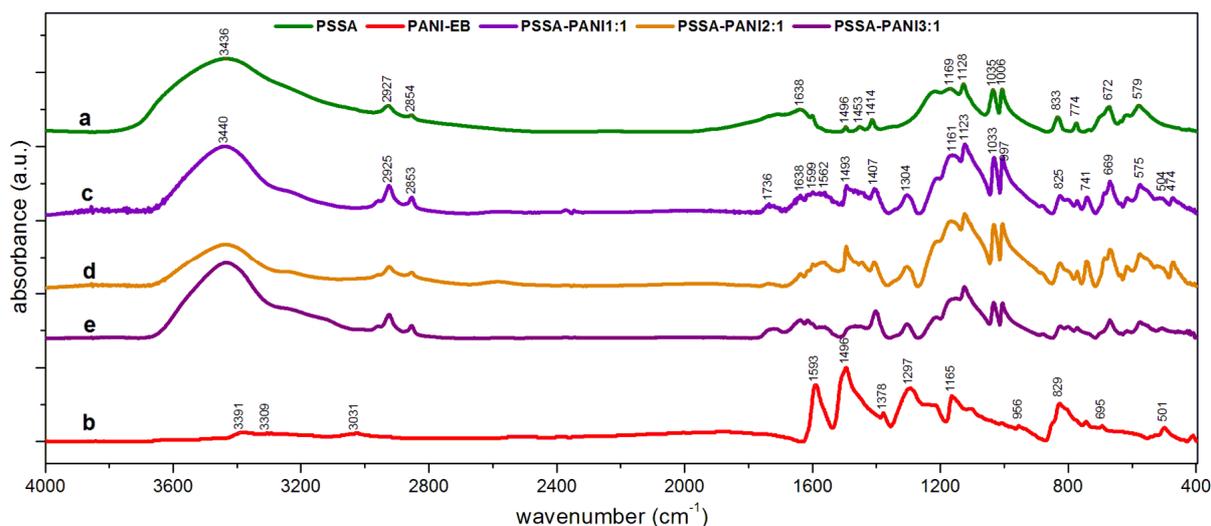
Fig. 3. Recorded FT-IR spectra of (a) PSSA, (b) PANI-EB, (c) PSSA-PANI 1:1 composite, (d) PSSA-PANI 2:1 composite, (d) PSSA-PANI 3:1 composite

In the spectra recorded for PSSA-PANI composite (Fig. 3.c-e) almost all peaks charactersitic to PSSA and PANI are clearly visible, with the exception of those masked by the wider or larger intensity peaks as in case of –N–H stretching vibration (3384 cm^{-1}) which is present in case of PANI-EB but masked by the wide peak located at 3440 cm^{-1} due to the presence of water in the investigated sample. A series of characteristic peaks of PSSA and PANI-EB are displaced in case of PSSA-PANI composites which is most probable due the interactions occurred during the polimerisation of anyline in aqueous PSSA medium. The C-N stretching vibrations at 1297 and 1378 cm^{-1} in PANI-EB appear displaced (1304 and 1407 cm^{-1}, respectively) due the vicinity of SO$_3$H groups. Also C=C stretching in the quinoid ring (1593 → 1599 cm^{-1}) and aromatic ring in plane deformation (1006 → 997 cm^{-1}) appeared displaced as their positioning is different in prepared PSSA-PANI. The situation is similar in case of all prepared PSSA-PANI ratios composites. The presence of groups at ~1562 cm^{-1} and 1493 cm^{-1} characteristic to N-benzenoid and quinoid ring respectively emphasizes of a polymer in its conductive form. The peak at 1496 cm^{-1} could denote a π-electron delocalization degree due the protonation of PANI. IR spectra of the polyaniline shinthesized in the presence of PSSA at three molar ratios confirm the presence of Emeraldine salt – conducting polyaniline.

Fig. 4 presents the TG and DTG derivatograms recorded for PANI-EB, PSSA and PSSA-PANI (at three molar ratios). Also, thermal stability of PSSA-PANI at different molar ratios were analyzed and compared to those of PSSA and PANI-EB.

By analyzing the data in derivatograms recorded for PSSA, it can be distinguished three ranges of mass loss. The first one, from 50 to 130 °C, is attributed to water loss, the second range, 299–350 °C, corresponds to the decomposition of sulphonil groups, while the third one, 390–450

°C, is due to the decomposition of the main chain in polymer. As regards PANI-EB, the significant mass loss (43.5%) begins around the value of 470 °C and continues up to 581 °C due to the degradation processes of polymeric chain.
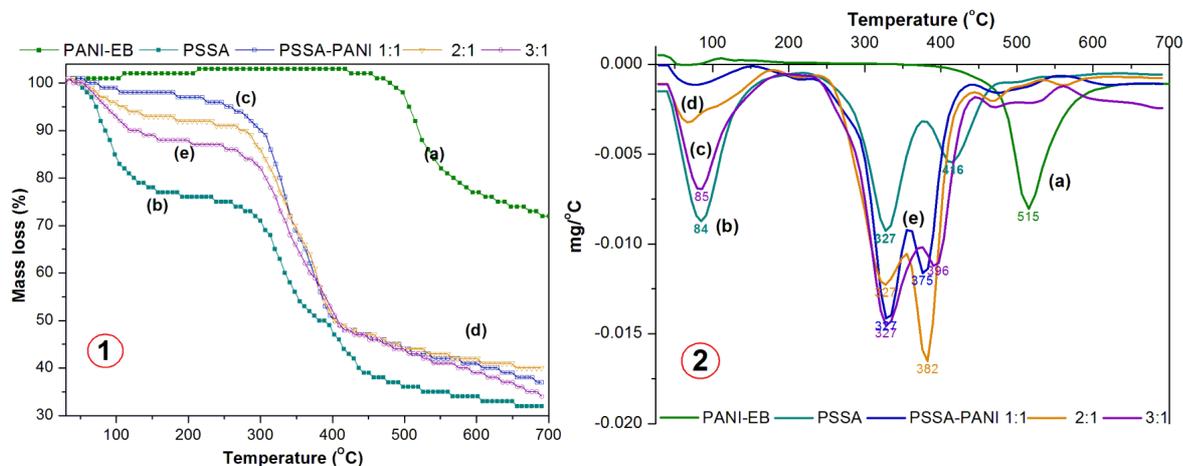
Fig. 4. Recorded TG (1) and DTG (2) patterns for (a) PANI-EB, (b) PSSA and PSSA-PANI at (c) 1:1, (d) 2:1, (e) 3:1 molar ratios

Data recorded in case of PSSA-PANI at all three molar rations indicate an important mass loss since the first degradation stage, which might be explained by the presence of water due to PSSA hygroscopicity. Thus, from 50 to 160 °C the following mass losses occur: 3.27% (1:1), 8.79% (2:1), 13.21% (3:1). Significant discrepancies can be noticed in the following two stages of degradation. For the range 289–330 °C there were recorded mass losses of about 28 % for the ratios 1:1 and 2:1, and 15 % for 3:1 ratio. In case of the stage between 343 and 425 °C, mass loss values are 22 % (1:1), 15 % (2:1), and 25 % (3:1) respectively, and peak degradation temperature (T_{peak}): 1:1 (379 °C) < 2:1 (409 °C) < 3:1 (425 °C). Higher values of decomposition temperature were recorded in case of sample synthesized using higher concentration of sulphonate polystyrene. Mass losses of about 4–5 % are emphasized in the last decomposing stages that can be assigned to the degradation of the base chain and substituent sulphonate groups in polystyrene [28]. For all the investigated products, the degradation process is not complete. In each case there is a residue varying between 35.89 %, for 1:1 PSSA-PANI, and 39.59 %, for 3:1 PSSA-PANI. Comparing data obtained for the three mixtures with those of the native polymers it can be noticed a sufficiently high thermal stability. The property is improved with reducing the amount of PSSA in the initial mixture.

Fig. 5 presents the images recorded by scanning electron microscopy (SEM) of PSSA and PANI-EB, as well as those of PSSA-PANI at the three mentioned molar ratios. These images indicate completely different morphologies, rough in case of PANI (Fig. 5a), and very smooth in case of PSSA (Fig. 5b). The different aspect of the two polymers is determined by the fact that PSSA is an amorphous polymer while PANI is a highly crystalline one. The morphology of the three films obtained with PSSA-PANI modifies as a function of the molar ratio (Figs. 5c-e). It can

be noticed that with the increase of the ratio in favor of PSSA, the surface aspect changes from unregulated, which is specific to PANI, towards a smooth one, which is common to PSSA.

(a) (b)

(c) (d) (e)
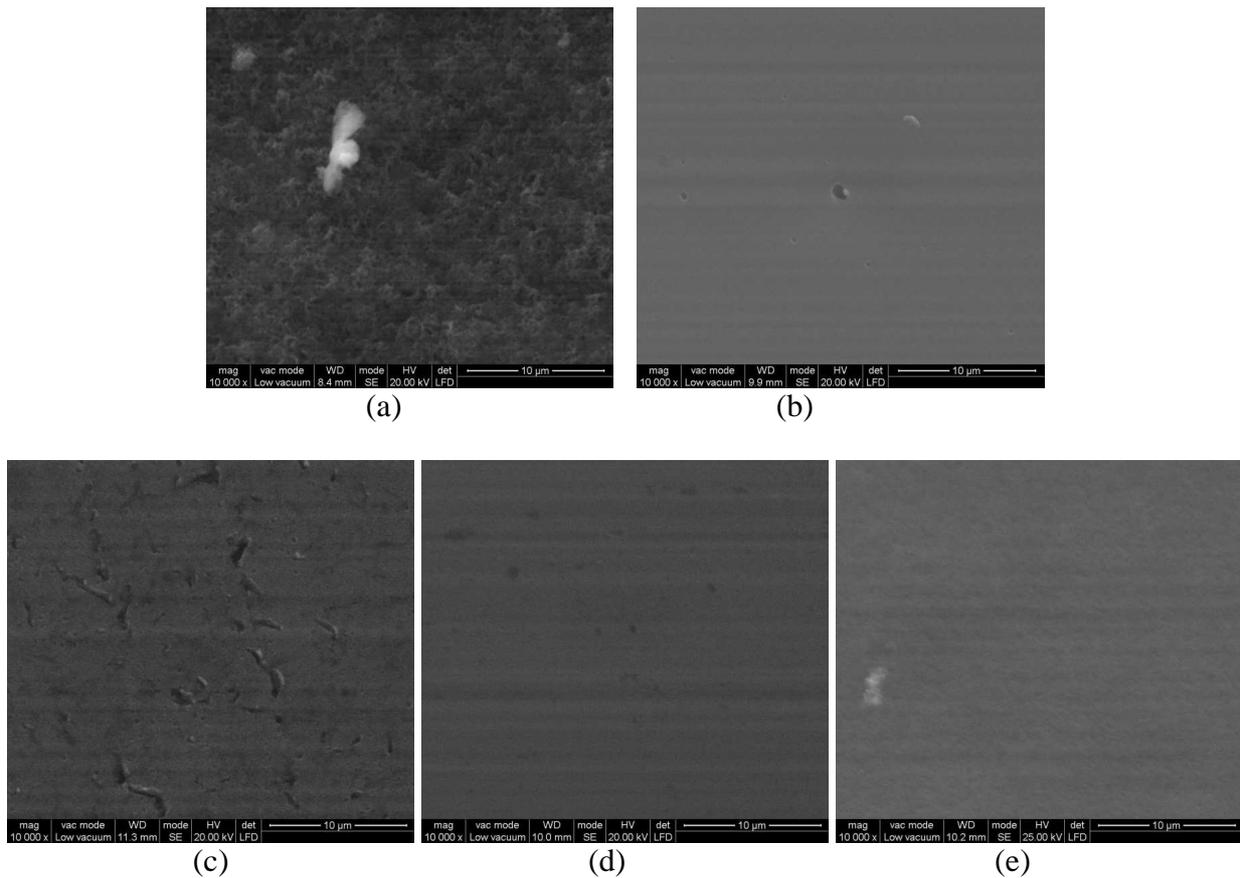
Fig. 5. Recorded SEM micrographs for (a) PANI-EB, (b) PSSA,
PSSA-PANI (c) 1:1, (d) 2:1, (e) 3:1

The morphology of PSSA-PANI films at the three molar ratios were analyzed by atomic force microscopy (AFM). Fig. 6 shows the three-dimensional images (3D-AFM) of the surfaces of thin layers deposited by spin coating. The recorded images pinpoint to the obtaining of some relatively smooth films of PSSA-PANI and confirm the conclusion obtained by means of SEM analysis. Likewise, it can be observed that as the PSSA percent increases, the surface irregularities of the obtained films diminish. They practically reduce from 0.21 μm in case of PSSA-PANI 1:1 to 62 nm for PSSA-PANI 3:1.

(a) (b) (c)
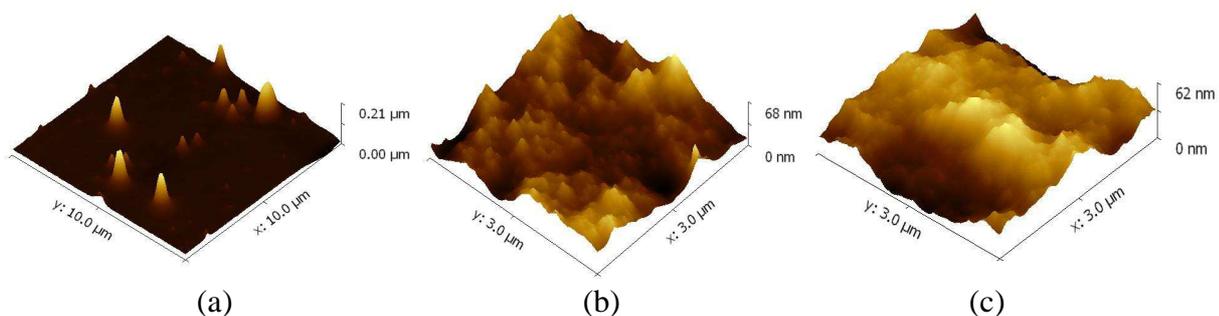
Fig. 6. Three-dimensional images (3D-AFM) in case of thin layers obtained with PSSA-ANI at different molar ratios: (a) 1:1, (b) 2:1, and (c) 3:1 respectively

2. Preliminary study regarding the compatibility between CdSe NC's and polymer matrix

One of the difficulties in introducing or deposition of thin layers of CdSe nanocrystals optically active is to achieve efficient energy transfer by ensuring mobility of charge carriers at the interface between the polymer layer and electrically electroemisive layer of nanocrystals. Nanocrystals prepared through colloidal synthesis are typically surrounded by ligands which do not ensure effective transfer of the carriers. The use of these ligands in the process of synthesis of of CdSe nanocrystals is necessary to obtain high emission quantum yields, avoiding their agglomeration and to ensure a uniform size distribution. Ligands used typically are the saturated monocarboxylic fatty acids (octanoic acid, myristic or stearic acid), oleic acid or TOPO. They do not ensure an efficient carrier transfer, nor are compatible with electrically conductive polymer layers. The study highlighted the opportunity tu use pyridine or derivatives as compatible ligands

A number of compatible ligands have been tested, such as pyridine and its derivatives, 2-aminopyridine and 4-aminopyridine. The ligand exchange of CdSe nanocrystals after synthesis thereof followed by re-dispersed in chloroform or n-hexane provides a high degree of processability of the solution to obtain electroemisive thin layer attached to the polymeric layer acting as charge carrier transport. Testing afforded pyridine derivatives of CdSe nanocrystals surrounded by ligands 2 or 4-aminopyridine which has the advantage of them by means of the functionalization of amino groups and to establish additional connections with the transport layers of electrons and holes in the composition of the electroluminescent cell. The experimental procedures aimed at obtaining a first phase through a method for synthesizing colloidal nanocrystals of CdSe using CdO, oleic acid, TOPO, selenium powder and TBP as precursors for the reaction of synthesis parameters are optimized in order to obtain a size distribution and suitable fluorescent emission. CdSe nanocrystals obtained has been investigated by techniques XRD, TEM, fluorescence spectroscopy. After separation from the reaction medium and purification of CdSe nanocrystals, ligands are exchanged by bringing it in a mixture of n-hexane-pyridine nanocrystals prepared. The exchange of the ligands occurs at temperatures of approx. 90 ° C, in a reaction vessel equipped with reflux under a protective atmosphere of nitrogen. After precipitation and separation of CdS nanocrystals surface having attached pyridine were re-dispersed in n-hexane. Experimental procedures are aimed at the evaluation stage 4-aminopyridine introduction at the stage of CdSe nanocrystals synthesis thus allowing elimination phase ligand exchange. To ensure a smooth movement of charge carriers and increased density photoemission has experienced centers compaction layer CdSe nanocrystals having pyridine surface modified by exposure to high pressure glass or PET substrate that was previously submitted layers bakery and CdSe nanocrystals PSSA. Compacting was carried out under nitrogen, in a pressure vessel at 70-80 bar for a period of approx. 24 hours.