U.P.B. Sci. Bull., Series B, Vol. 69, No. 2, 2007 ISSN 1454-2331

INNOVATIVE METHODS TO ADVANCE IN NEW MATERIALS DESIGN; ELECTROCHEMICAL BEHAVIOUR OF POLYANILINE – POLYPYRROLE COMPOSITE COATINGS OBTAINED BY ELECTROSYNTHESIS

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În această lucrare prezentăm o metodă computațională bazată pe tehnicile mecanicii moleculare (MM) şi dinamicii moleculare (MD) pentru investigarea omogenității şi izotropiei materialelor, precum şi o metodă electrochimică pentru investigarea comportamentului electrochimic al materialelor şi pentru validarea rezultatelor obținute prin metoda computațională.

S-au realizat modele pentru masa amorfă a amestecurilor polianilină (PANI) – polipirol (PPY). S-au efectuat două iterații, prima utilizând o simulare MM pentru echilibrare, a doua utilizând simulări MD pentru rafinarea modelului. Pentru a evalua comportamentul mecanic al modelelor s-au efectuat teste virtuale de tracțiune uniaxială prin procedura derivatei a doua (SD).

Compozitele PANI-PPY au fost formate prin oxidare electrochimică în mediu acid, utilizând soluții de diferite compoziții. Materialele obținute au fost caracterizate prin voltametrie ciclică, teste de conductivitate cu două sonde precum şi măsurători de solubilitate. Ambele abordări au arătat că materialele formate se comportă ca un material nou cu caracteristici superioare. În ceea ce priveşte investigarea computațională, in urma rafinarii, sistemele simulate s-au prezentat omogene şi aproximativ izotropice. Cu ajutorul testelor electrochimice, s-a arătat că structura, morfologia şi eficiența acoperirilor sunt dependente de raportul inițial al monomerilor (anilina şi pirol) şi de potențialul aplicat. De asemenea, s-a arătat că noile materiale compozite se comportă foarte diferit față de homopolimerii corespunzători.

In this work we present a computational method based on molecular mechanics (MM) and dynamics (MD) techniques, to investigate materials homogeneity and isotropy as well as an electrochemical method to investigate the

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electrochemical behaviour of the materials and also to validate the results gathered using the computational method.

Amorphous bulk models of polyaniline (PANI) – polypyrrole (PPY) mixtures were generated. Two steps have been performed iteratively, the former using a MM simulation for equilibration and the latter using MD simulations for model refinement. Virtual uniaxial traction tests were performed, adopting the Second Derivative (SD) procedure, in order to assess the mechanical behaviour of the bulk models.

Composites of PANI and PPY have been formed by electrochemical oxidation in acidic medium using feed solutions with different compositions. Further the new materials have been characterized by means of cyclic voltammetry (CV), two-probe conductivity and solubility measurements. Both approaches showed that the formed material behaves as a new material with enhanced characteristics. Concerning the computational investigation, after refinement the simulated bulk systems were homogeneous and approximately isotropic. By means of electrochemical investigations it was shown that the structure, yield and the morphology of the coatings were dependent on the feed ratio of monomers (aniline and pyrrole) and the applied potential. It was shown also that the behaviour of the new composite materials is very distinct and different with the respect of the homopolymers.

Keywords: polyaniline, polypyrrole, composite, computational methods, organic coatings

1. Introduction

In recent years, and particularly as a result of the developing semiconductor technology, the search for organic materials exhibiting electronic conductivity has become an active subject of study by both chemists and physicists. Various polymers were synthesized exhibiting electronic conductivities in their oxidized or reduced states. Polymeric organic conductors were classified by Metzer et al. [1] in five systems.

All the polymers in these systems possess π-electron systems; otherwise they could not be conductive. In their pure state they are usually not conductive, but some of them may have semiconductive properties. They become conductive upon doping by suitable chemical or electrochemical oxidations. By the process of doping they undergo injection of electrical charges into their main chains. These charges may be either positive or negative. Polypyrrole, polyaniline and derivatives are easily prepared by anodic oxidation methods [2 – 4].

Conductive organic polymers may be useful for a number of practical applications, for example, light weight energy storage devices (solar batteries) and in electronic circuitry applications [5].

Electrochemical synthesis of conductive polymers allows preparation of layers of polymers of desired thickness and shapes generally not possible by chemical methods [6].

The most promising conductive polymers have been those made from monomers of pyrrole, thiophene, aniline and benzene. These polymers can be easily prepared electrochemically in organic or aqueous solutions. Conductivities are usually in the semiconductor range [10^{-9} to 10^{-2} S cm^{-1}]. In general, the method of electrolysis affects to a great extent the electrical and physical properties of the polymer [7]. Polypyrrole (PPY) does not require added dopants to be conductive [8].

This polymer switches between a black conductive form and a yellow nonconductive form by changing the applied potential on the underlying electrode so as to reduce or oxidize π-electron network of the polymer.

In spite of different oxidation potentials of aniline (0.8V vs. SCE) and pyrrole (1.2V vs. SCE), the literature suggests that simultaneous oxidation and codeposition of polyaniline and polypyrrole is possible [9, 10].

The aim of this paper is to investigate and discuss the results of molecular modelling for PANI-PPY composites using a computational method based on MM and MD techniques in order to predict the behaviour of composite material, concerning the homogeneity, isotropy and miscibility. The paper also presents the experimental results regarding the synthesis of the coatings of PANI-PPY composites on platinum substrates using galvanostatic and potentiodynamic methods. The electrochemical properties of these composite coatings were studied by CV.

2. Experimental

2.1. Electrochemical procedure

Pyrrole and aniline monomers were purchased from Merck and used as received.

Electro-polymerization and electrochemical tests were carried out on a 173 model EG&G Princeton Applied Research Potentiostat/Galvanostat. A single compartment electrochemical cell was used. The counter electrode was a platinum wire and saturated calomel electrode was used as reference electrode. All experiments were run at 25°C. All solutions were prepared with freshly distilled water.

Polyaniline, polypyrrole and PANI-PPY films were electropolymerized onto a platinum wire substrate of 0.45 cm^2 surface area by applying galvanostatic impulses. The polymerization was carried out in a 0.05M monomer + 0.5M H_2SO_4 electrolytic solution. Before each experiment, the working electrode was cleaned by reducing flame.

The concentration of one monomer was maintained constant at 0.05M and the proportion in moles of the other one was varied from 0.05M to 0.01M. Thus, the initial concentration of the monomers (aniline and pyrrole) was varied from 1:1 to 5:1. The electrochemical characteristics of the coatings were studied by cyclic voltammetry using 0.25M Na_2SO_4 aqueous solution. The working electrode potential was cycled on the potential range of -1000 mV up to +1000 mV, with a scan rate of 20 mV s^{-1}.

2.2. Modelling procedure

Molecular simulations were carried out using particularly the commercial MS Modelling 4.0 software (Accelrys Cambridge, UK); molecular mechanics and molecular dynamics simulations were performed.

Polymer bulk models

For some of the composite materials the composition independent computational bulk models of mixtures with 1:1 and 3:2 (w/w) PPY-PANI ratios were generated employing the Amorphous Builder. The bulk models containing the polymer chains (the applied techniques of building and equilibration of polymeric chains are completely described elsewhere [11, 12]) were grown at 300K under the cubic periodic boundary conditions using COMPASS force field.

The polymer model is based on the features of the real material concerning; crystallinity, tacticity, and regioselectivity. The materials were simulated in both air (dielectric constant equals 1) and implicit water environment (dielectric constant equals 4).

In order to allow the building of a 3-D amorphous periodic cell and to reduce computational costs, the molecular weight of the polymeric chains for PANI and PPY was reduced by two orders of magnitude. Table 1 summarizes the details of the simulated bulk models properties: blend composition, side length of the packing cube, and number of atoms of the model.

The side length of the packing cubes was chosen in order to fulfil three mutually offsetting requirements:

1) the cell has to be wide enough to avoid interactions between atoms and their periodic images;
2) the number of polymeric chains has to be high enough to allow random three dimensional orientation and, hence, an actual homogeneous behaviour of the model;
3) the number of atoms in the periodic cell has to be as low as possible in order to reduce computational costs.

Table 1

Main features of bulk models

Model	Composition of the blend (w/w)	No. of repeated unit of the chain		No. of chains	No. of atoms in the model	Dielectric constant	Density of bulk model (g/cm^3)	Dimensions of the model (Å)
		PPY	PANI					
PPY-PANI	3:2	964	1032	2	1996	1	1	29.62
PPY-PANI	3:2	964	1032	2	1996	4	1	29.62
PPY-PANI	1:1	800	1204	2	2004	1	1	29.60
PPY-PANI	1:1	800	1204	2	2004	4	1	29.60

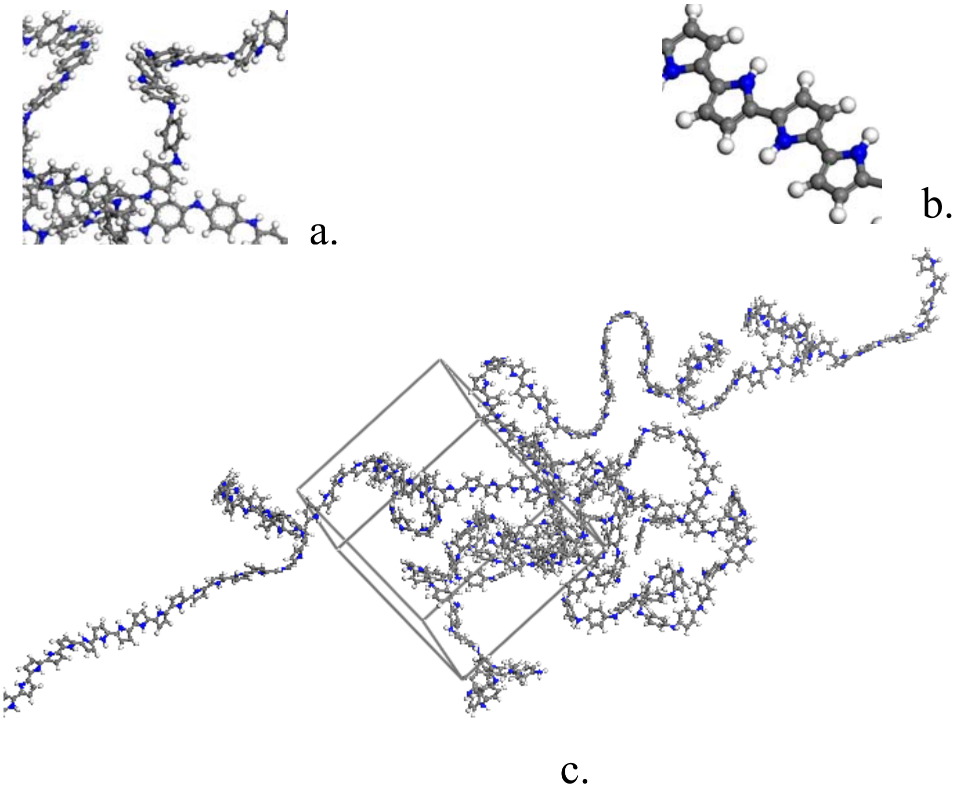


Fig. 1. (a) PANI chain; (b) PPY chain; (c) periodic bulk model with periodic boundary conditions, containing one chain of PPY and one chain of PANI.

Model Refinement

The constructed polymer chains must show both a distribution of conformation angles and a global chain geometry representative for the simulated material. In order to optimize initial geometries and repairing poor geometries for built bulk models two steps were performed. First, the equilibration by means of molecular mechanics simulations and further the model refinement by means of molecular dynamics simulations were done. Moreover, as Hofmann and co-workers suggested [11, 13], the conformation energy and non-bond energy were properly scaled in order to have chains redistribution within the periodic cell. A sequence of five steps of Minimizations and Molecular Dynamics calculations was performed, each being characterized by different scaling factors as depicted in Table 2.

Table 2

Force field scaling factors for amorphous packing refinement procedure

Scaling Factor	Bond	Non-bond
Step 1	0.01	0.01
Step 2	0.1	0.01
Step 3	0.1	0.1
Step 4	1	0.1
Step 5	1	1

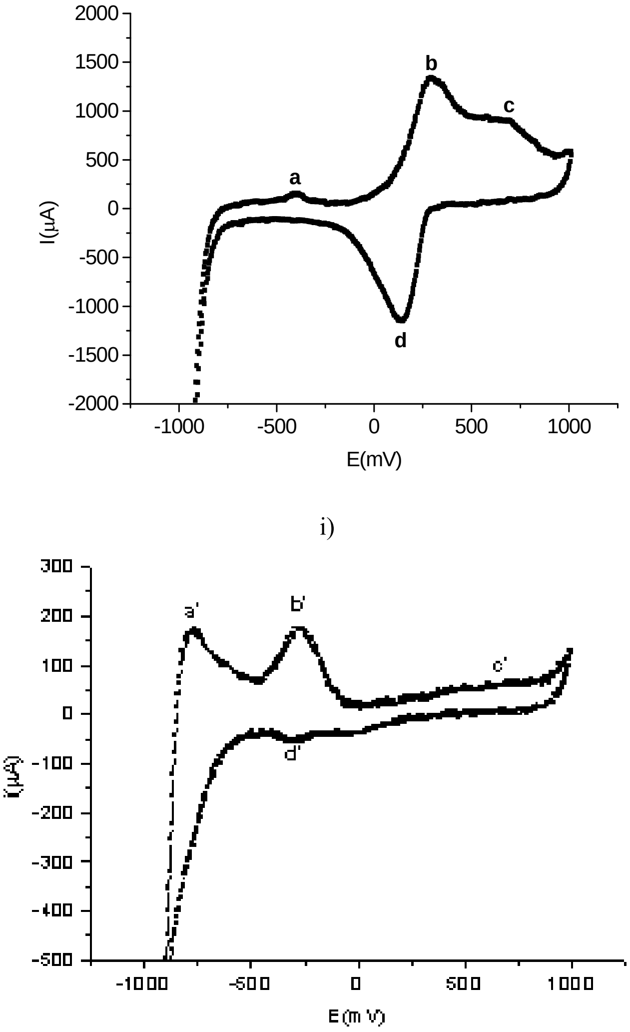
All initial packing models were subjected to extensive equilibration procedure using the newly developed COMPASS force field. Each step of minimization was performed using two different algorithms. Initially Steepest Descent algorithm was used since it is an extremely robust method most likely to generate a lower-energy structure. Generally applied for the first 10-100 steps of minimization, the Steepest-Descent method was used in the case of initial relaxation because the gradients were large and the configurations were far from the minimum. Afterwards, the most advanced Conjugate gradient-Fletcher-Reeves algorithm (that can be unstable if the conformation is so far away from a local minimum) was used to achieve efficient convergence to the minimum. The NVT MD simulations were performed at 300 K for each constructed and minimized bulk model. For the NVT ensemble, the number of molecules N, volume V and temperature T of the system are kept constant. MD calculations simulate the natural motions of all atoms in a polymer system over time at non-zero temperature and the MD algorithm makes use of the classical Newton equation of motion. Each dynamic calculation was kept on running until the dynamic equilibrium of the system was achieved. In order to ensure that the simulations are carried out for sufficient time, which is one of the most important criteria in equilibrating the system, the number of steps of NVT MD simulations was 300,000 (300 ps). The time step was equal to 1 femtosecond. In order to reduce computational costs it is common to use a suitably cut-off distance for non-bond interactions; therefore for this study a cut-off distance of 9.5 Å was used. In order to obtain a realistic bulk model of a homogeneous and amorphous material, two conditions must be fulfilled: uniform distribution and random orientation of polymeric chains inside the periodic cell. Building the bulk model, the software does not take into account these features, but only geometric criteria. For this reason it was necessary a series of dynamic simulations to reach the isotropy of the cell. The cell isotropy was evaluated testing the mechanical properties of the model using the Mechanical Properties Assessment tool.

3. Results and Discussions

Electrochemical synthesis of PANI-PPY films starting from different precursor solutions produces adherent black films. They show a great electroactivity in the cycling solution.The voltammetric profiles are very similar in the potential values of the current peaks, being located at intermediate values of the typical electrochemical responses of the homopolymers; this means that a new material with new characteristic properties was obtained.

Figs. 2 (i) and (ii) show the cyclic voltammograms for polyaniline (PANI) potentiograms obtained in a cycling solution of 0.25M Na_2SO_4 at different cycles – first and third, respectively (in order to observe the changes in the film stability). First, the PANI films on the platinum substrates in a synthesis solution of 0.05M aniline + 0.5M H_2SO_4 by galvanostatic method were obtained. Characterization of the PANI obtained films was made by cyclic voltammetry in a solution free of monomer, in this case we used an aqueous solution of 0.25M Na_2SO_4.

It is well known that polyaniline can exist in three different oxidation states such as leucoemeraldine (fully reduced form), emeraldine form (partially oxidized form) and pernigraniline (fully oxidized form). At the anodic potential sweep the oxidation forms of polyaniline are obtained and on the anodic branch of the cyclovoltammogram the oxidation peaks (a, b, c) appear. At the reverse potential sweep on the cathodic branch of the cyclovoltammogram appear the reduction peaks (see Fig. 2 (i)), and finally the hydrogen evolution. Once the number of cycles increases, the shape of the cyclovoltammograms changes.



i)

ii)

Fig. 2. The cyclic voltammograms of PANI/Pt modified electrode in 0.25M Na_2SO_4 at a scan rate of $20mVs^{-1}$:
i) the first cycle and ii) the third cycle

Thus, Fig. 2 (ii) presents the cyclovoltammogram of PANI/Pt modified electrode obtained at the cycle number 3. One can see that in these cases appear two anodic oxidation peaks: the peak (a') is due to the anodic oxidation of hydrogen and the peak (b') represents the anodic oxidation of the reduced form of polyaniline (leucoemeraldine base) to the partially oxidized form (emeraldine base). On the cathodic branch of this cyclovoltammogram only a reduction peak (d') appears, which represents the reduction of the oxidized forms of PANI to leucoemeraldine base. Analyzing the Figs. 2 (i) and (ii) one can see with the increasing of cycles number a significant decrease of the peak heights, a decrease of the peaks number and a shift to more electronegative potentials.

Further we studied the behaviour of PPY/Pt modified electrode prepared from an aqueous solution of 0.05M pyrrole + 0.5M H_2SO_4 using the galvanostatic method. Fig. 3 shows the cyclovoltammogram of PPY/Pt modified electrode in 0.25M Na_2SO_4 electrolyte.

The broader peaks suggest complicated redox processes for PPY/Pt modified electrode, related to a counter – ion insertion. Thus, the HSO_4^- anion inserted in the polymer matrix would interact with the oxidized sites of the polymer chain. This would change the redox potential of the polymer by the formation of a mixed chain, part of it interacting with HSO_4^- anions that neutralize the positive charges of polypyrrole backbone and another one remaining positively charged.

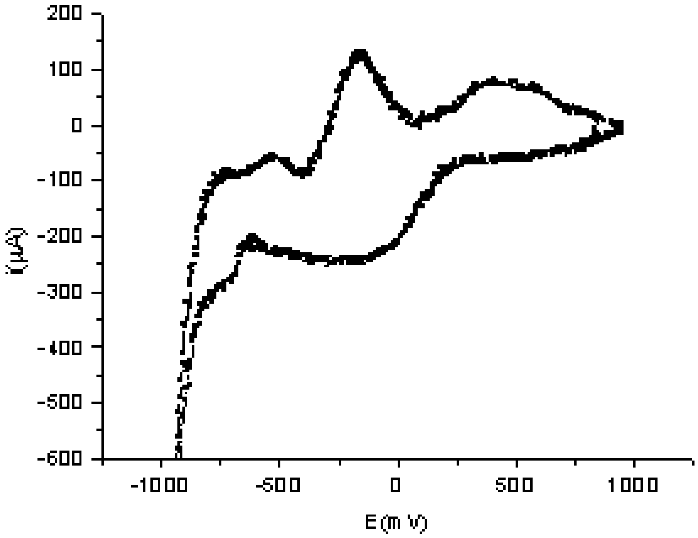


Fig. 3. The cyclic voltammogram of PPY/Pt modified electrode obtained at the cycle number 3 in 0.25M Na_2SO_4 at a scan rate of $20mVs^{-1}$

The oxidation and the reduction peaks of the first redox couple correspond to the following process:

$$PPY^{+}/A^{-} \underset{-e^{-}\text{ (oxidation)}}{\overset{+e^{-}\text{ (reduction)}}{\rightleftharpoons}} PPY/A^{-}$$

where A^- is an anion, in this case HSO_4^- ion.

Correspond to the insertion of the cation M^+ from the electrolyte forming the following adduct: $PPY/A^-/M^+$: The oxidation and reduction in the second step (see Fig. 3):

$$PPY/A^{-}/M^{+} \underset{+e^{-}\text{ (reduction)}}{\overset{-e^{-}\text{ (oxidation)}}{\rightleftharpoons}} PPY^{+}/A^{-}/M^{+}$$

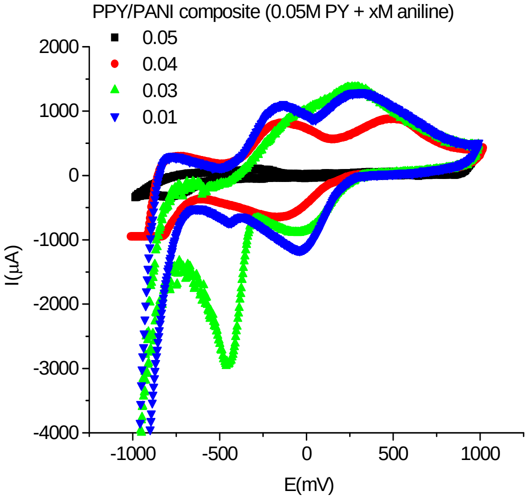
PPY films demonstrate a good stability on electrochemical cyclability.

Further, we have studied the formation of polyaniline – polypyrrole composite coatings on platinum substrate using the galvanostatic method. It was shown that the electrochemical properties of these coatings were dependent on the feed ratio of monomers (aniline and pyrrole) and the applied potential.

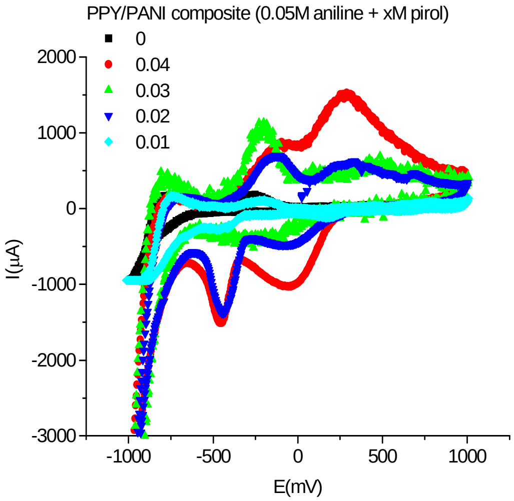
Figs. 4 (i) and (ii) illustrates the cyclic voltammetric behaviour of the PANI-PPY composite films prepared by using two different series of synthesis solutions: 0.05 pyrole +(0.01-0.05)M anilive and 0.05M aniline + (0.01-0.05)M pyrrole.

The cyclic voltammograms from Fig. 4 (i) show an enhaced electroactivity in 0.25M Na_2SO_4 electrolyte with the current peaks located at intermediate values of the typical electrochemical responses of the homopolymers (see Tables 3 and 4). Similar behaviour of PANI/PPY composites was recorded when the monomers ratios in synthesis solution were changed. We analyzed the Figs. 4 (i) and (ii) and we have concluded that the electrochemical response of the new composite material is not the simple addition of those related to PANI and PPY. This fact would be an indication of the formation of a new material.

In general, it can be shown that the shape of the cyclic voltammograms is strongly influenced by the molar feed ratio of monomers – see Figs. 4 (i) and (ii) and Tables 3 – 4.



i)



ii)

Fig. 4. The cyclic voltammograms of the i) PANI/PPY and ii) PPY/PANI composite films obtained at the cycle number 3 in 0.25M Na_2SO_4 cycling electrolyte at a scan rate of $20mVs^{-1}$

Table 3

The kinetic parameters of the PANI/PPY composite films obtained at the cycle number 3 in 0.25M Na_2SO_4 at a scan rate of $20mVs^{-1}$

xM aniline	ipa$_1$ (mAcm^{-2})	Epa$_1$ (mV)	ipa$_2$ (mAcm^{-2})	Epa$_2$ (mV)	ipc$_1$ (mAcm^{-2})	Epc$_1$ (mV)	ipc$_2$ (mAcm^{-2})	Epc$_2$ (mV)
0.01	1.10	-150	1.30	300	0.73	-440	1.17	-30
0.02	1.00	-120	1.35	280	1.60	-460	0.96	-50
0.03	0.90	-95	1.40	250	2.95	-445	0.87	-40
0.04	0.83	-140	0.90	490	0.65	-160	0.03	450
0.05	0.18	-260	0.07	800	0.04	-280	0.03	100

Table 4

The kinetic parameters of the PPY/PANI composite films obtained at the cycle number 3 in 0.25M Na_2SO_4 at a scan rate of $20mVs^{-1}$

xM pyrrole	ipa$_1$ (mAcm^{-2})	Epa$_1$ (mV)	ipa$_2$ (mAcm^{-2})	Epa$_2$ (mV)	ipc$_1$ (mAcm^{-2})	Epc$_1$ (mV)	ipc$_2$ (mAcm^{-2})	Epc$_2$ (mV)
0.01	0.11	-215	0.09	806	0.27	-480	0.11	190
0.02	0.70	-130	0.60	305	1.38	-440	0.50	-40
0.03	1.10	-200	0.56	446	0.39	-250	1.02	-50
0.04	0.87	-100	1.50	280	1.50	-460	0.03	100
0.05	0.18	-260	0.07	800	0.04	-280		

It was shown in the modelling part of the paper that in recent years MM and MD approaches represent a useful tool to evaluate physical and chemical properties of polymeric materials, such as surface and bulk properties. In particular, the computational approach adopted here allows the evaluation of the miscibility of the two polymers, assessing the homogeneity and isotropy of the new material.

At the end of the refinement procedure an amorphous volume element with random and homogeneous distribution of polymeric chains was expected (as you can see in Fig. 5). In order to test the miscibility of the two polymers and abtained random and homogeneous distribution of the polymeric chains it was chosen to test the mechanical properties, using the Elastic Properties Analysis tool in the Discover module.

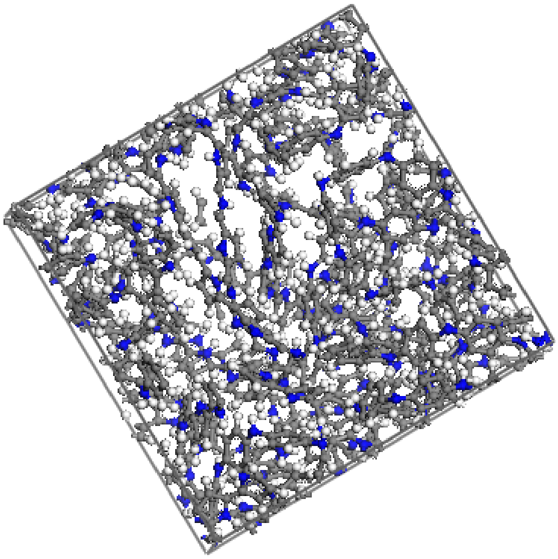


Fig. 5. Homogeneous and isotropic bulk model of PPY-PANI after the refinement procedure.

The virtual uniaxial traction tests were performed on the 3-D cubic cell along its three perpendicular edges and, assuming the linear elasticity theory, the elastic stiffness matrix was calculated. Finally, by reversing this matrix, the compliance matrix elastic module referred to the three perpendicular direction of the cell (Exyz averaged) were obtained.

Table 5

The mechanical properties deduced using computational bulk models

Model	Composition of the composite (w/w)	Dielectric constant	Ex (GPa)	Ey (GPa)	Ez (GPa)	Eavg (GPa)
PPY-PANI	3:2	1	0.0421	0.0535	0.0452	0.0470
PPY-PANI	3:2	4	0.8305	1.4176	0.9237	1.0572
PPY-PANI	1:1	1	0.3124	0.2815	0.3584	0.3174
PPY-PANI	1:1	4	1.7170	1.6357	1.7199	1.6908

The results of the mechanical properties assessment presented in Table 5 showed that for each composite, the values of the Young module along the three perpendicular directions are very similar; the difference between them being lower than 10%. This means that the polymeric chains redistribute themselves in a random and homogeneous way inside the volume element.

Concerning numerical values of elastic constants, likely low stiffness of the composites were achieved: materials like those simulated in this work present Young module at the same orders of magnitude with the obtained values. As a limitation of the models is the fact that the models are very small (characteristic dimensions around 30 Å) although mechanical properties are related, at least for polymers, to macro-scale features: atomistic model do not take into account micro-holes. However, mechanical properties were assessed in order to validate the model's isotropy and not the stiffness of the composites.

4. Conclusions

The cyclic voltammograms of the polypyrrole films and polyaniline films displayed clearly discernible oxidation and reduction peaks.

The electrochemical response of the obtained PANI/PPY composite films is not the simple addition of those related to PANI and PPY; this fact represents an indication of the formation of a new material with different properties.

Taking into account the computational results we can say that Molecular Modelling provides accurate and essential data on composite materials based on PANI-PPY. The results of the mechanical properties assessment for each composite model showed that polymeric chains redistribute themselves in a random and homogeneous way inside the volume element. This technique reveals a composite with properties different from those obtained by simple addition of the two polymers. We can say that the computational results confirmed the electrochemical ones and moreover they provided additional information regarding the composite homogeneity. There are different ways to evaluate the homogeneity and the miscibility of these materials and further investigation are on running.

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