Multiscale Molecular Modeling and Laboratory Investigation of Polypyrrole-polyaniline Composite

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Atomistic molecular modeling based on forcefield simulations, dissipative particle dynamics (DPD) mesoscale computational method and electrochemical techniques are here used to investigate the mechanical properties, structural morphology and electrochemical response of poly(pyrrole) (PPY)- poly(aniline) (PANI) conductive polymer composite. Computational bulk models of PPY-PANI were implemented at atomistic- and meso-scale and composite films were made available by electropolymerisation on platinum support. Further data concerning mechanical properties, structural morphology and electrochemical response of PPY-PANI composite films were collected by means of in silico investigations, scanning electron microscopy (SEM) and cyclic voltammetry (CV). Both approaches showed that the new formed composite material behave as new material with enhanced characteristics when compared with single component. Concerning material morphology and mechanical properties, simulated bulk systems were homogeneous and their Young's moduli ranged from 0.04 to 0.475 GPa depending on the material composition. Based on CV measurements, it is stated that the electrochemical activity, reversibility, electrical conductivity and cycle-life stability of the PANI-PPY composite is significantly higher than the pure conducting polymer.

Keywords: PPY-PANI films, atomistic- and meso-scale modeling, mechanical testing, electrochemical properties

In recent years, as a result of semiconductor technologies development, the search for new polymeric materials exhibiting electronic conductivity has become an active subject of study by both chemists and physicists. Nowadays, various conductive polymers are being developed for many uses such as corrosion inhibitors, compact capacitors, antistatic coating, electromagnetic shielding and smart windows which are capable to vary the amount of light to pass [1-2]. However, limitations such as insolubility and poor mechanical strength are barriers for mass production [2-3]. Several attempts have been made to overcome conductive polymers limitations an example is blending of a conductive polymer such as poly(pyrrole) (PPY), poly(aniline) (PANI) or poly(thiophene) *etc*., with an insulating polymer such as poly (vinyl alcohol) or poly(vinyl chloride) *etc*., in aqueous or organic medium [4-6]. The produced conductive polymer composites encompass conducting properties related to the conductive polymer with enhanced stability and mechanical strength reinforcement. However, a decrease of the conductivity of the conductive polymer composites was observed when conductive polymers are blended with insulating polymers. We attack the problem of improving stability, mechanical strength and at the same time maintaining the conductivity by combining two conductive polymers PPY and PANI. Among the conductive polymers, PPY and PANI are the most noted for their excellent thermal and electrical stability properties and these place them as promising candidates to be used for the design of improved conductive polymer composites [7]. PPY is one of this new generation polymeric materials. It has been the main focus due to advantages such as environmentally stable, ease to synthesis and relatively high conductivity [8]. PANI captured the attention of the scientific community due to its high electrical conductivity, ease of synthesis, environmental stability, and simple doping/dedoping chemistry [9-10].

Atomistic and mesoscale molecular modeling techniques are new and powerful methods for polymeric materials investigation at molecular level and have proved to be able to supply macroscopic characteristics such as mechanical properties, structural morphology *etc.*, [11-13]. The atomistic modeling of polymers for calculating mechanical properties has been researched for several years. A static method was developed early by using molecular mechanics (MM) techniques [14]. Stress–strain simulations in molecular dynamics (MD) have been employed for some time [15]. Most atomistic simulations of polymers involve amorphous linear polymers and the chain lengths are typically oligomeric in scale and flexible. Polymeric chains such as PPY and PANI have complex molecular architecture and only limited amount of research has been conducted due to difficulties in constructing realistic bulk models for such materials [16]. A new method was developed recently for building atomistic structures [14]. This method involves the instantaneous construction of systems containing one or more types of polymer and /or small molecules starting from single polymer chain and /or single molecule. This basic method has been implemented in Material Studio commercial software and is here used for atomistic simulations of PPY-PANI structure [14].

Depending upon the spatial dimensions of the system and properties under investigation computer modeling of polymeric materials can range from forcefield based molecular dynamics (mechanical properties) to mesoscale simulation methods (material morphology) [11-15]. Dissipative Particle Dynamics (DPD) is one of the most known mesoscale simulation approach; it is based on bead-spring approach and has traditionally been used to investigate structural morphology of polymers in solutions, melts and blends [11].

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In this work PPY-PANI composite material with different compositions was studied by atomistic, mesoscale molecular modeling and electrochemical techniques.

A protocol which allows the assessment of the mechanical properties of the material and the dependency of the mechanical properties as a function of PPY and PANI content was set-up using forcefield based simulations.

Another aim of this study was to develop a protocol at mesoscale based on DPD approach to assess the structural morphology of PPY-PANI composite with different compositions.

From experimental point of view materials were made available by electropolymerisation and were further investigated concerning the electrochemical response by means of CV and material structural morphology by means of scanning electron microscopy. Eventually, atomistic and mesoscale models were validated against experimental data.

Experimental part

Materials and methods

Molecular simulations were carried out using the commercial Materials Studio 4.0 software (Accelrys Cambridge, UK).

Computational methods: realization of polymer bulk models at atomistic scale

The repeating unit of PPY is available as standard model in Material Studio. Conversely, the repeating unit of PANI was built manually and then minimized in order to obtain a stable structure. The polymeric chains were then generated starting from the repeating units using "Built Polymers" tool from Material Studio. Finally, bulk models of PPY-PANI, which consist of a periodic cubic box with a characteristic dimension of about 3 nm containing about 2000 atoms, were generated. Computational models of PPY-PANI were implemented, with different compositions: 0.9:0.1, 0.7:0.3, 0.5:0.5, 0.3:0.7, and 0.1:0.9 molar ratios. The different compositions of bulk models are obtained by varying the number of monomers for each of the two mentioned chains. All the models were built so that they are 100% amorphous, PANI chain completely atactic and PPY chain syndiotactic, with head-tail connections. The models density was set 1.2 g/cm^3. Initial geometries were refined on the basis of the procedure previously adopted by [16] which consists on equilibration by means of molecular mechanics and further model refinement by means of molecular dynamics simulations. The refinement procedure was composed of five steps. Each step consisted of a preliminary minimization, which lasted until a 10^{-4} gradient was reached for all of the system energy terms and of a NVT (constant number of atoms, volume and temperature) molecular dynamics simulation performed in order to simulate a 300 ps time lapse with a time step of 1 fs. In each step, the energy terms were scaled by using proper scaling factors, whose values were equal to 0.01 during the first refinement step and were progressively increased up to one in the subsequent four steps. During MD simulations a 300K temperature was simulated and controlled by means of the Berendsen thermostat. The COMPASS forcefield was employed to model the energy system.

The cells isotropy and elastic moduli were evaluated using the Mechanical Properties Assessment tool. Virtual uniaxial traction tests were performed on computational models on three perpendicular directions. Further, second derivative (SD) procedure was adopted in order to assess the mechanical behavior of the bulk models. SD procedure allows the calculation of symmetrical elastic stiffness matrix, which was inverted and further Young moduli were calculated.

Computational methods: realization of polymer bulk models at mesoscale

First chemically distinct species of the system were identified, thus the underlying chemistry of the material is not lost. PPY-PANI system contains two types of polymeric chain therefore the number of chemically distinct units is two and were represented by beads of different types. Each monomer molecule was assumed to be a bead and each simulated polymeric chain consists of about 50 beads (50 monomer molecules). Each bead is subject to three non-bonded forces from its neighbors: a conservative force ($\boldsymbol{F}^{C}_{ij}$), a random force ($\boldsymbol{F}^{R}_{ij}$) and a dissipative force ($\boldsymbol{F}^{D}_{ij}$). The total force on a bead $\boldsymbol{f}_i$ is showed as:

$$f_i = \sum_{i \neq j} (F_{ij}^C + F_{ij}^D + F_{ij}^R) \quad (1)$$

where, the sum runs over all other beads within a certain cutoff radius. In order to calculate conservative forces, Van Krevelen solubility parameter (δ), [18], was determined using Quantitative Structure Property Relationship (QSPR) tool available in the Material Studio software. From Van Krevelen solubility parameters were derived Flory Huggins parameters (χ), according to eq. 2 and the values are depicted in table 1:

$$\chi = \frac{V_{ref}(\delta_i - \delta_j)}{RT} \quad (2)$$

where:

V_{ref} is the molar volume of the monomers (table 1),

R - universal gas constant (8.3145 J/mol*K);

T - the temperature. Subsequently, Flory-Huggins parameters were converted into repulsion parameters (a_{ij}).

Repulsion parameters describe the conservative forces between pairs of interacting beads and were assessed assuming Groot and Warren approach [19] which is a linear relationship between χ and a_{ij} (eq. 3).

$$a_{ij} = \frac{\chi}{0.306} + 25 \quad (3)$$

Table 1
VAN KREVELEN SOLUBILITY PARAMETER, MOLAR VOLUME, FLORY-HUGGINS INTERACTION PARAMETERS AND REPULSION PARAMETERS FOR THE SPECIES OF THE SYSTEM

Species	Van Krevelen parameter ((J/cm^3))$^{-0.5}$	Molar volume (cm^3/mol)	Flory-Huggins parameter		Repulsion parameter	
			PPY	PANI	PPY	PANI
PPY	21.80	52.90	0.021	0.05	25	25.07
PANI	20.89	75.53	0.05	0.021	25.07	25

Table 2
YOUNG'S MODULI VALUES ALONG THE THREE ORTHOGONAL DIRECTIONS AND AVERAGED VALUE FOR EACH BULK MODEL

Model	Composition of the blend [M]	Ex [GPa]	Ey [GPa]	Ez [GPa]	Eavg [GPa]
PPY-PANI	0.3:0.7	0.4750	0.3954	0.4731	0.4478
PPY-PANI	0.5:0.5	0.3124	0.2815	0.3584	0.3174
PPY-PANI	0.7:0.3	0.0421	0.0535	0.0452	0.0470

Repulsion parameters used in the DPD calculation are depicted in table 1. Dissipation parameters (γ) were set to 4.5 reduced units (r.u.) [19]. Computational mesoscale cubic models of PPY-PANI with characteristic dimensions of 10x10x10 r.u. (~60 nm) and characteristic molar ratios of 0.9:0.1, 0.7:0.3, 0.5:0.5, 0.3:0.7, 0.9:0.1 were implemented with periodic boundary conditions and were equilibrated for 100,000 steps, with a time step equal to 0.05 r.u.. DPD calculation module was further employed to explore and visualize the distribution of polymeric chains within the mesoscale computational bulk models.

Experimental methods: realization of composite polymer films

A model 173 EG&G Princeton Applied Research Potentiostat/Galvanostat was used for the electrochemical polymerization. Electropolymerization was done in a single compartment electrochemical cell. As the counter electrode a platinum wire was used. A saturated calomel reference electrode was used as the reference electrode. As the oxidation potential of aniline (0.8V *vs*. saturated calomel electrode (SCE)) and pyrrole (1.2V *vs*. SCE) are very near, we believe that simultaneous oxidation and codeposition of PPY and PANI is possible by changing the applied potential.

PANI-PPY films were made available by electropolymerization onto a platinum wire substrate by applying galvanostatic impulses (current density of 0.3 mA/cm^2 for a time period of 20 min). The polymerization was carried out in a 0.05M monomer + 0.5M H_2SO_4 electrolytic solution. In the case of the synthesis of composite films, the concentration of monomer was maintained constant at 0.05M and the proportion in moles of pyrrole was varied from 0.05M to 0.01M. It can be observed that, 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. The cycling solution was 0.25M Na_2SO_4. The working electrode potential was cycled on the potential range of -1000mV up to +1000mV, with a scan rate of 20mV/s. Further investigations concerning PPY-PANI films morphology were performed by means of Scanning Electron Microscopy (SEM).

Results and discussion

Computational methods; characterization of atomistic polymer bulk models

Virtual traction tests and SD procedure were applied to assess the Young's moduli values along three perpendicular directions of PPY-PANI composite system with different compositions. Young's moduli numerical values ranged from 0.04 to 0.475 GPa and Poisson's ratio raged from 0.2856 to 0.31. The numerical values of elastic constants depend on the material composition. Molecular modeling investigations revel that an increase of PANI content in the composite material leads to a higher enhancement of the mechanical properties of composite material PPY-PANI (table 1). The obtained numerical results respect theoretical criteria (theory of linear elasticity) and are in good agreement with data from the literature which showed that Young's moduli for PANI ranged from 0.04 to 0.7 GPa [20] while the Young's moduli for PPY ranged from 0.04 to 0.53 GPa [21]. However, precise evaluation of the reliability of MM and MD to assess mechanical properties of PPY-PANI can be completed by *ad hoc* experimental tests. The major limitation of the computational technique at atomistic scale used in this work is related to the restricted time scale and model size which can be simulated. However, despite this limitation MD simulations provide reliable trends of the mechanical properties as a function of the material composition.

Computational methods; characterization of mesoscale polymer bulk models

Using mesoscale DPD tool PPY-PANI models with different compositions were implemented and structural morphology was computed. A preliminary estimation of the structural morphology of PPY-PANI systems was performed by assuming Flory-Huggins theory [22-23] which predicts that components with similar δ values lead to small repulsion and should mix. Accordingly PPY (δ=21.80 (J/cm^3)$^{-0.5}$) should mix well with PANI (δ=20.89 (J/cm^3)$^{-0.5}$). As expected, PPY readily mix with PANI and the composite system displays the morphology of an homogenous material after 20,000 steps of DPD calculations. Figure 1 illustrates typical morphologies for PPY-PANI composite with different compositions 0.9:0.1 (fig. 1a), 0.7:0.3 (fig. 1b), 0.5:0.5 (fig. 1c), 0.1:0.9 (fig. 1c) molar ratio. These represent equilibrium structures after a simulation time of 100,000 steps, corresponding to a real time of ~5μs. All computational bulk models present uniform and random distribution of polymer chains. The homogeneity of the PPY-PANI composites observed by means of mesoscale simulations (fig. 1) is closely mirrored by materials morphology as apparent in SEM micrographs (fig.2b). In conclusion, we can say that mesoscale simulations, such as DPD, allow *in silico* experiments to be easily and cheaply performed on complex polymeric materials such as PPY-PANI requiring as input only the molecular structure of the constituents. Through several initial runs, it was verified that is possible to compute the morphology of PPY-PANI material with just few hours of CPU time, while atomistic molecular dynamics display significant results over runs of 2-3 ns, which can take weeks of simulations time. However, the DPD methodology comes with its own set of approximations, especially involving the coarse graining space and time. Extracting physical value of time, beads and computational bulk models dimensions requires careful interpretation.

Table 3
KINETIC PARAMETERS OF THE PPY-PANI (0.05M PPY-xM PANI) COMPOSITE FILMS 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

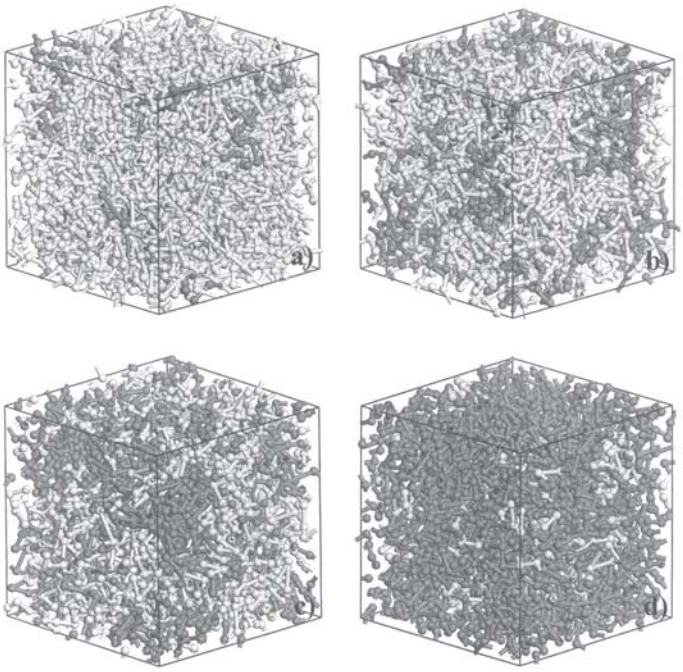

Fig. 1. Equilibrium morphologies of PPY-PANI composite. The light grey chain denote PPY chain and the dark grey chain denote PANI chain. The image a), is the equilibrium configuration of PPY-PANI 0.9:0.1, b) is the equilibrium configuration of PPY-PANI 0.7:0.3, c) is equilibrium configuration of PPY-PANI 0.5:0.5. and d) is equilibrium configuration of PPY-PANI 0.1:0.9(molar ratio). The images show the systems after 100,000 steps of DPD calculation. The polymeric chains have migrated uniformly and randomly within the computational model and display an homogenous morphology of the material

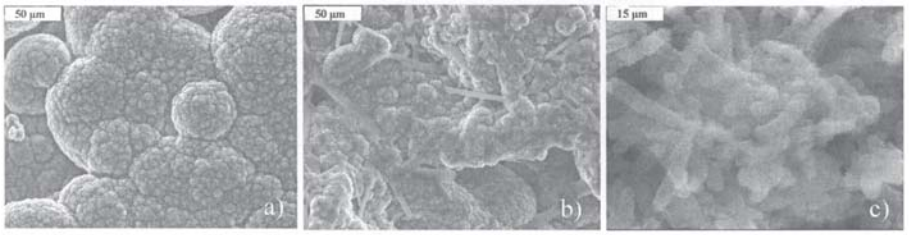

Fig. 2. SEM images of pure PPY a), composite PPY-PANI (0.7:0.3 M) b) and pure PANI c)

Experimental methods: characterization of polymer composites

Since the oxidation potential of aniline (0.8V *vs*. SCE) and pyrrole (1.2V *vs*. SCE) are very near, simultaneously oxidation and codeposition of polyaniline and polypyrrole was possible by changing the applied potential.

The SEM micrographs of PPY, PPY-PANI (0.7:0.3M) and PANI polymeric films are given in figure 2. For the PPY pure sample a cauliflower type structure can be observed in the micrograph (fig. 2a), PANI pure sample displayed a fibers type structure (fig. 2c). The composite material PPY-PANI (fig. 2b) appeared to be composed by both cauliflower type structure and fibers type structure with an approximately homogeneous distribution. A similar behaviour was observed for PPY-PANI films with different compositions.

For what concern the electrochemical response, PPY-PANI composite showed significant changes in electrochemical behaviour when compared with the homopolymers. Figure 3 illustrates the cyclic voltammetric behaviour of the PPY-PANI composite films that were prepared on platinum substrate in manner described in experimental section. Analyzing this figure one can see

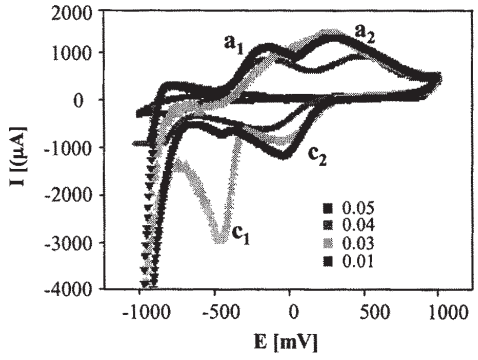

Fig. 3. The cyclic voltammograms of the PPY-PANI (0.05M PPY-xM PANI) composite film obtained at the cycle number 3 in 0.25M Na_2SO_4 at a scan rate of $20mVs^{1}$

that the behaviour of the current – potential curves is a function of the molar feed ratio of monomers. The cyclic voltammograms from figure 3 show a great electroactivity in 0.25M Na_2SO_4 as supporting electrolyte, the potential values of the current peaks being located at intermediate values of the typical electrochemical responses of the

homopolymers (table 3). This fact would be an indication of the formation of a new material with differentiated and improved properties. In general, it can be shown that the behaviour of the current – potential curves is very much influenced by the molar feed ratio of monomers – see for comparison kinetic parameters given in table 3.

Conclusions

Two types of investigation were carried out; atomistic and mesoscale molecular modelling and experimental approach to assess the mechanical properties, morphology and electrochemical behaviour of PPY-PANI composite material, both methods lead to similar results.

The results of the virtual mechanical tests showed that PPY-PANI bulk models are characterized by Young's moduli of 0.04-0.475 GPa, in good agreement with experimental results available in the literature, therefore atomistic molecular modelling is an useful tool to assess the mechanical behaviour of PPY-PANI composite.

Mesoscale simulations evidenced the formation of an homogeneous composite material. These results are confirmed by experimental investigations (SEM) hence, DPD method provide very accurate and detailed structural and morphological description on PPY-PANI composite material.

The excellent conductivity combined with appropriate stability placed PPY-PANI as promising material for applications such as conductive polymeric material.

The combination of independent and complementary investigations, molecular modelling and experiments, provide a detailed picture of the physicochemical behaviour of the materials. Nevertheless, molecular modelling can act both as a guide and as tool to experimenters prior to perform costly assays or to assess certain characteristics.

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