Molecular Modeling of Electrical Conductive Polymer-Polymer Composites

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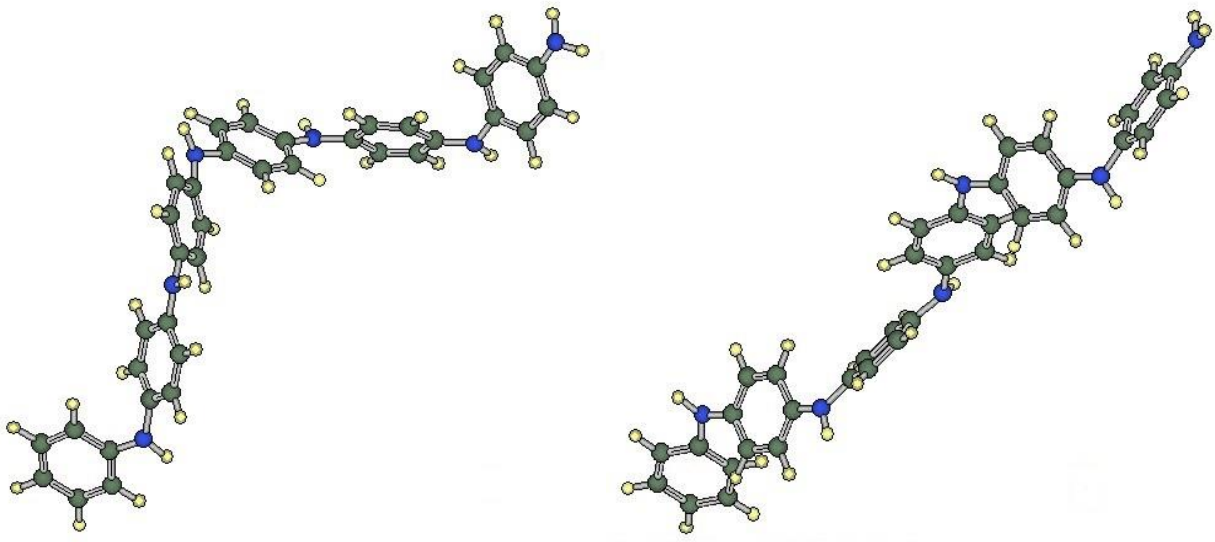
Abstract – Polymer-polymer composites based on polyaniline and water-soluble polymers were obtained. It is shown that intermolecular hydrogen bonds are formed between the composite components. The energy of hydrogen bonds is determined. The intermolecular interaction between the components of the polymer-polymer composite affects it on the physicochemical parameters.

Keywords – polyaniline, polymethacrylic acid, polyvinyl alcohol, hydrogen bonds, electrical conductivity.

Polymer-polymer composites (PPCs) based on the electrical polymer polyaniline (PANI) and film-forming polymers: polyvinyl alcohol (PVA) and polymethacrylic acid (PMAA), have properties that allow them to be used to produce various devices. Such PPCs are effective corrosion inhibitors and composites that are able to form electrical wires on surfaces of different nature. The study of the PPCs by X-rays has shown that intermolecular hydrogen bonds may be formed between the components, which will affect the physical and chemical properties of the studying composites. Thermo mechanical studies indicate the intermolecular interaction between polymers macromolecules that are part of the PPC. The thermo mechanical curves of individual polymer are significantly different from the PPC curves.

The modeling of intermolecular interaction between the macromolecules of the PANI and the water-soluble polymer was studied by quantum-chemical method. Quantum-chemical calculations for polymer fragments of PMAA (8 units) and PANI (4 protoned links) and their compositions were performed using the MOPAC2016 program and the Winmostar graphical interface, using the RM7 semi-empirical method, taking into account the dielectric permeability of water (EPS=78.4) . Thermodynamic calculations of the models were made using the key parameter THERMO(290,330,10).

The calculations of the structure of macromolecules indicate that PANI, PVA, PMAA can form many conformations.



a b

Fig.1. Conformation of polyaniline macromolecules: a) compressed spiral, b) rod.

In the formation of the PPC, the interaction between macromolecules of different types occurs with the formation of a composite. During the formation of the composite conformation of macromolecules may change. Thermodynamic calculations made it possible to estimate the energy of intermolecular hydrogen bonds and the length of these bonds. The average energy of hydrogen bonds is 13.0 kJ/mol and 4 - 5 bonds are formed by 6 units of PMAA. Depending on the structure of fragments, the amount and energy of hydrogen bonds may change. For example, the table provides a calculation for thermodynamic parameters for a PANI, PVA and a composite on their basis.

Table

Thermodynamic parameters for a PANI, PVA and a composite on their basis

Temperature, K	Heat of formation, $\Delta_f H^o$, kJ/mol	Entalpium, H, kJ/mol	Heat capacity, C_p, J/mol·K	Entropy, S, J/mol·K
Thermodynamic parameters for 10 links of polyvinyl alcohol				
290	-2463.16	83.024	522.07	840.88
298	-2458.33	87.337	546.33	855.56
300	-2457.75	88.370	549.98	859.22
310	-2452.15	93.919	567.92	877.55
320	-2446.38	99.792	585.85	895.86
330	-2440.43	105.74	603.75	914.16
Thermodynamic parameters for 6 polyaniline units				
290	1558.33	90.49	582.15	918.01
298	1563.06	95.21	596.30	934.06
300	1564.24	96.41	501.08	938.07
310	1570.35	102.51	619.90	958.08
320	1576.64	108.81	638.61	978.06
330	1583.13	115.29	657.18	997.99
The sum of the parameters of polyvinyl alcohol and polyaniline				
290	-904.82	173.52	1114.22	1758.90
298	-891.78	182.55	1143.69	1789.61
300	-893.49	184.84	1151.06	1797.24
310	-881.79	196.54	1187.82	1835.63
320	-869.74	208.60	1224.46	1873.92
330	-857.31	221.03	1260.92	1912.16
Thermodynamic parameters for composite				
290	-973.02	159.64	1070.20	1376.30
298	-969.34	168.32	1100.13	1405.83
300	-967.13	170.53	1107. 61	1413.22
310	-955.86	181.79	1144.78	1450.14
320	-944.23	193.46	1182.35	1487.08
330	-932.22	205.44	1219.36	1524.03

The calculated heat capacity for PVA, PANI and their composite increases with temperature. The total heat capacity of the PVA and the lady is greater than the heat capacity of the composite with the same composition of fragments. The difference between the corresponding values is 41.56 - 44.45 J/mol·K. Enthalpy values for PVA, PANI and composite

with temperature grow. The difference between the sum of the corresponding values of the PVA and the lady and the calculated value for the composite is 13.88 - 15.59 kJ/mol. This fact may also indicate the formation of hydrogen bonds between PVA and PANI in the resulting composition. Similar studies were conducted for a composite based on PMAA and PANI. As in the case of the composite of PANI-PVA, it was noted that intermolecular hydrogen bonds are formed between the macromolecules, the energy of which is different and the lengths of this bond may also change. The lengths of the ligaments are respectively 3.07, 1.97 and 2.04 Å. It can be argued that the energy of the first bond will be the lowest. The energy of the average second bond will be the highest, and the energy of the third bond will accept some average.

In Fig.2a-2d are given PPC models formed by PANI-PMAA and PANI-PVA with calculated of electrostatic potentials surfaces.

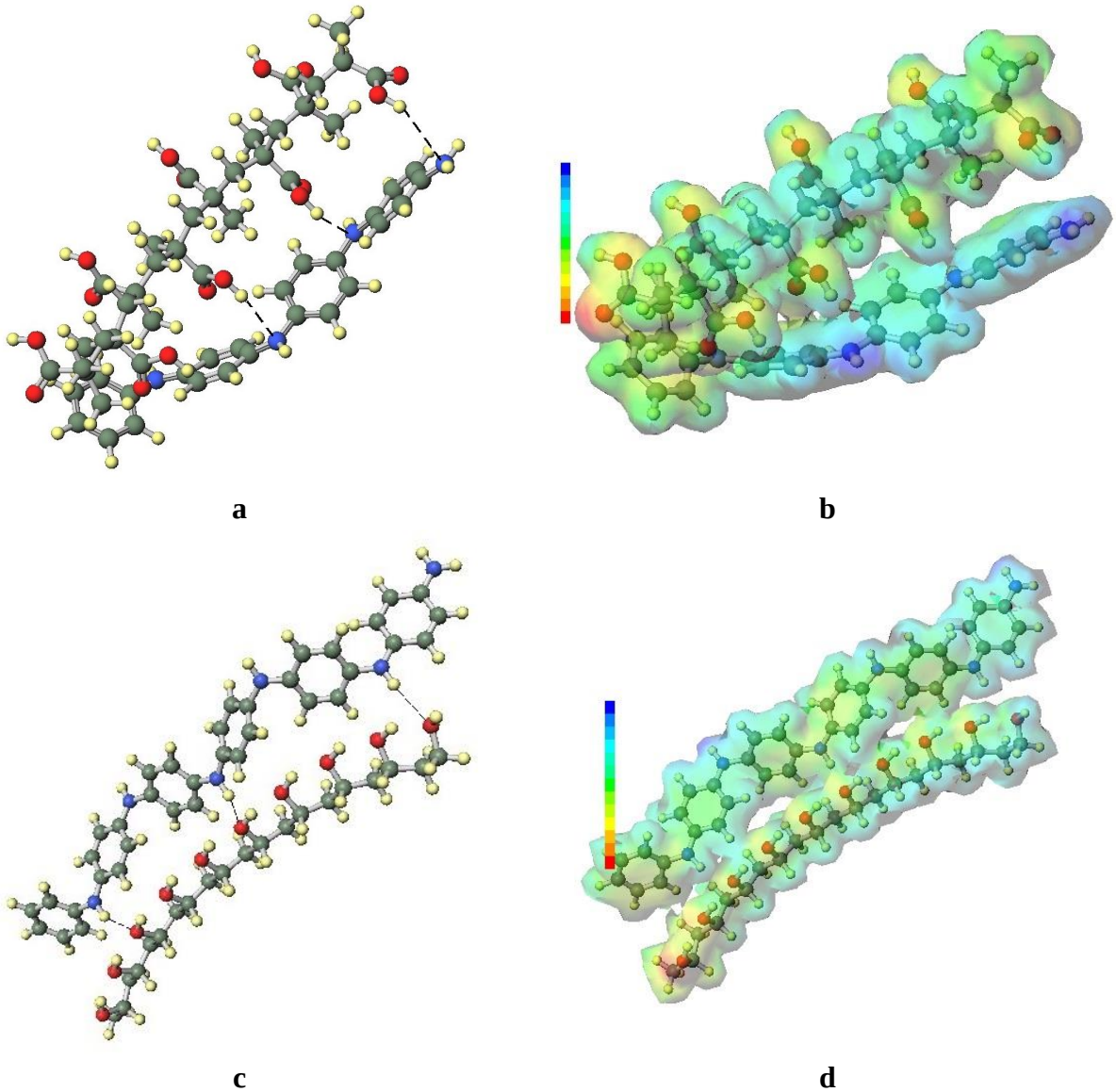


Fig. 2. Model of polymer-polymeric composite of PMAA-PANI (**a**, hydrogen bonds marked with a dotted) and surface of ESP Population Charge (**b**); and PVA-PANI (**c**, hydrogen bonds marked with a dotted) and surface of ESP Population Charge (**d**).

The formation of hydrogen bonds between the components of the polymer-polymer composite affects the physic-chemical parameters of the PPCs. The specific electrical conductivity of the studied PPCs and its dependence on temperature were found.