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Simulation of pyrolysed polyacrylonitrile based composite with amorphising boron additives

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Abstract. The paper deals with the possibility of modifying pyrolyzed polyacrylonitrile with amorphizing additives. Adsorption features of the boron atom on the surface of the monolayer of polymer are studied, and the geometric and electron-energy characteristics of the composite obtained are established. The calculations were performed using the semi-empirical MNDO method within the framework of the molecular cluster model.

1. Introduction

Nanomaterials have received much recent attention [1-3], which is determined by two reasons. Firstly, small-sized crystallites are reported to increase reactivity in solid-phase reactions, such as sintering processes. Secondly, substances in a nanocrystalline state display special properties (magnetic, optical, etc.) that arise due to quantum-size effects and are uncharacteristic of bulk materials [4-5]. Therefore, the preparation and study of nanocrystalline materials is challenging for production of new generation devices. To obtain a new material, a detailed examination of its structure, calculation of the geometric characteristics, careful description of the physical and chemical properties are required. To achieve this goal, computer simulation methods are widely employed in nanotechnology [6-8].

Modern development of industry necessitates creation of new materials, including amorphous metals. Metallic glasses or amorphous metals are novel engineering alloys in which the structure is not crystalline (as it is in most metals) but rather is disordered, with the atoms occupying more-or-less random positions in the structure. In this sense, metallic glasses are similar to the more familiar oxide glasses such as the soda-lime glasses used for windows and bottles. A noticeable ordering in amorphous metals extends only to a few interatomic distances. As far as the properties are concerned, a number of amorphous metals display significantly different ones as compared to crystalline metals of similar composition [9].

Due to the structure, amorphous metals possess a number of unique properties: they have higher tensile yield strengths and higher elastic strain limits, improved electromagnetic properties and corrosion resistance [10]. Materials possessing the above mentioned characteristics have a wide application as they can be used to produce new high-strength composites for aviation and astronautics. Due to the unique disordered atomic-scale structure, amorphous metals possess much better mechanical properties such as enhanced corrosion- and wear-resistance and magnetic performance and

Content from this work may be used under the terms of the Creative Commons Attribution 3.0 licence. Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI. Published under licence by IOP Publishing Ltd 1 as a result, amorphous metal-based materials have a wide range of application as coatings in chemical filters, vessels, electrodes [11-13].

However, it is known that the amorphous state of pure metals is characterized as unstable because upon heating, the process of crystallization begins. It is also reported that alloys of metals with additives of such non-metals as silicon, boron, carbon, phosphorus display much more stable characteristics as introduced elements called amorphous additives stabilize the amorphous structure.

Therefore, there is considerable interest in producing polimer matrix composites. Among these polymer matrices, pyrolyzed polyacrylonitrile can be used [14]. Incorporation of amorphizing additives to PPAN is regarded as the first step to preparation of a new nanomaterial, which is a PPAN-based composite with amorphous metals.

Using computer simulation methods, the preparation of a PPAN-based composite with amorphizing additives is examined. The interaction process between pyrolyzed polyacrylonitrile and boron, chosen as an amorphizing element, was studied. The calculations were performed within the framework of the molecular cluster model using the semi-empirical MNDO method [15-16].

2. Pyrolyzed polyacrylonitrile as a matrix for amorphous metals

Pyrolyzed polyacrylonitrile [17], that is used as a matrix base, is obtained from polyacrylonitrile under IR heating. Polyacrylonitrile (PAN) has a wide range of physical and chemical properties and diverse applications. Also, the advantage of this material is its low cost and simple preparation [18-19]. When a polymer is exposed to electromagnetic radiation in the IR range, a synergistic effect is observed that accelerates polymer conversion on the basis of self-organization principle. Under IR heating, PAN undergoes chemical and structural transformations, and a polyconjugated system forms with an increase in heating intensity. Simultaneously, the crystalline and amorphous phases in the PAN structure deplete and disappear, and pyrolyzed polyacrylonitrile (PPAN) with semiconductor properties forms (Figure 1).



Figure 1. Structural chemical modifications in PAN upon heating.

We hypothesise that sp1, sp2 and sp3 hybridization of carbon chemical bonds in the presence of nitrogen atoms in PPAN and the modification of its structure with various additives should lead to formation of new PPAN based materials with promising physical and chemical properties, such as electrical conductivity, optoelectronic properties, density, adsorption, electron work function, electromagnetic absorption, catalytic and sensory properties. These properties show good promise for the manufacture of power semiconductor devices, manufacture of highly pH- gas media CO2 sensitive gages, high-speed optical switches, indicators, oxidation catalysts for the manufacture of fuel cells, efficient heat sinks, high-density data recording and storage systems.

The complexing properties of the nitrile groups of pyrolyzed polyacrylonitrile have found application in the manufacture of nanocomposites. Metal composites with particles of cobalt, iron, copper, and silver have already been obtained [20-21].

It should be noted that the amorphous structure is fundamentally possible for all metals and alloys. For practical use, transition metal alloys (Fe, Co, Mn, Cr, Ni, etc.) are usually used, in which amorphous elements of B, C, Si, P, S types are added to form an amorphous structure. Amorphous alloys obtained in this manner usually contain about 80 % of one or more transition metals and 20% of

metalloids that are added to form and stabilize the amorphous structure. Amorphizers decrease the melting point and provide a sufficiently fast cooling of the melt below its glass transition temperature so, as a result, amorphous phase forms. The thermal stability of amorphous alloys is most affected by silicon and boron, alloys with boron and carbon have the greatest strength, and corrosion resistance depends on the concentration of chromium and phosphorus [22].

3. The MNDO calculation method

To study the structure of PPAN and characteristics of the interaction process with amorphous boron, we used the semi-empirical calculation method MNDO and the valence approximation method, i.e. unlike non-empirical methods, it takes into account only valence electrons in the atomic orbitals (AO) of valence shells. The influence of non-valent (core) electrons is implicitly taken into account in empirical parameters. In semi-empirical methods, Slater type orbitals are used to describe AO

$$\chi = Nr^{n-1}e^{-\xi r}Y_l^m(\theta,\varphi),$$

$$N = \frac{(2\xi)^{n+1/2}}{\sqrt{(2n)!}},$$

$$Y_l^m(\theta,\varphi) = (-1)^m \sqrt{\frac{2l+1(l-m)!}{4\pi(l+m)!}}P_l^m(\cos\theta)e^{lm\varphi}$$

where n, l, m are the principal, orbital and magnetic quantum numbers, N is the normalization constant, ξ is the Slater exponent, $Y_l^m(\theta, \varphi)$ is the spherical harmonic and $P_l^m(\cos\theta)$ is the adjoint Legendre polynomial. The value of ξ is usually chosen according to Slater's rules. The 2p_x orbital of a carbon atom has the following form:

$$\chi_{2p_{\chi}} = Ne^{-1.625r}\chi$$

The valence approximation means that only 1s AO is used for hydrogen, for elements of the second period of the Periodic table -2s, $2p_x$, $2p_y$, $2p_z$ AO. To find the eigenfunctions of the molecular orbital (MO) and the eigenvalues of the MO energies of the molecule's Hamiltonian, it is necessary to solve the Hartree-Fock-Rutaan equations:

$$\sum_{\nu=1}^{N} (F_{\mu\nu} - \varepsilon_i S_{\mu\nu}) c_{i\nu} = 0,$$
$$\mu = 1, 2 \dots N$$

Here, ϵ_{i-} single electron molecular orbital energy Ψi , $S\mu\nu$ – overlap matrix element, $F_{\mu\nu}$ – Fock matrix element:

$$F_{\mu\nu} = H_{\mu\nu} + \sum_{\lambda=1}^{N} \sum_{\beta=1}^{N} P_{\lambda\beta} \left[(\mu\nu|\lambda 6) - \frac{1}{2} (\mu\lambda|\nu 6) \right],$$

 $H_{\mu\nu}$ – core integral characterizing the electron energy in the field of nuclei:

$$H_{\mu\nu}=\int \chi_{\mu}(1)H^{sk}(1)\chi_{\nu}(1)dq_{1}$$

In semi-empirical methods, the approximation is introduced that differential overlap between the atomic orbitals μ and ν is equal to, $\chi_{\mu}\chi_{\nu}dq = \delta_{\mu\nu}\chi_{\mu}^2 dq$, $\delta_{\mu\nu}$ - Kronecker symbol. Then, two-electron integrals can be written as

$$(\mu\nu|\lambda\beta) = (\mu\mu|\lambda\lambda)\delta_{\mu\nu}\delta_{\lambda\beta}dq$$

This approximation turns a four-dimensional array of integrals $(\mu\nu|\lambda\zeta)$ into two-dimensional, which greatly reduces the number of integrals and, accordingly, the calculation time. In addition, three or

four AOs appearing in the integral $(\mu\nu|\lambda\zeta)$ belong to three or four different atoms (centers). Such integrals are called three- or four-center integrals and they are much more complicated to calculate than one-and two-center integrals. In semi-empirical methods, multicenter interaction integrals are assumed to be zero, which also significantly reduces the calculation time. The MNDO method takes into account inter electron repulsion integrals, including one-center overlaps. The integrals ($\mu\mu|\nu\nu$), $\mu\in A$, $\nu\in B$ are calculated, not approximated. An important advantage of the MNDO method is the rejection of parametrization of the resonance integral $\beta\mu\nu$ by the coupling type and the transition to the relation

$$H_{\mu\nu} = \delta_{\mu\nu} = S_{\mu\nu} \frac{1}{2} (\beta_{\mu} + \beta_{\nu})$$

The repulsion energy of the cores is calculated as

$$exp(-\alpha_{AB}R_{AB}) \rightarrow exp(-\alpha_{B}R_{AB}) + exp(-\alpha_{B}R_{AB}).$$

This replacement, as in the case of the resonance integral, reflects the peculiarity of the MNDO method, which consists in the rejection of the coupling parameters and the transition to the parameters of the atoms α_A and α_B .

The choice of the calculation method is determined by the results of the study of many high molecular weight solid structures that are in good agreement with the results of our experiment. A comparison of the obtained results with the calculation results obtained by using the molecular cluster model revealed a qualitative and quantitative agreement of the main conclusions, which allows us to consider the calculation results reliable.

4. Adsorption of B atom on the pyrolized polyacrylonitrile surface

As the object of study, a monolayer of PPAN of the composition $C_{44}N_{14}H_{10}$, i.e. nitrogen atoms comprise 20% of the total number of atoms. The distance between atoms in the layer is 1.4 Å. We studied the process of a boron atom adsorption on the surface of PPAN. It was found that adsorption takes place on the active centers, which are protrusions or depressions on the surface of the adsorbent, characterized by the presence of the so-called free valences. Therefore, we examined five positions of adsorbed boron atom on the surface of the polymer monolayer: 1) above a carbon atom, 2) above a nitrogen atom; 3) above the bond center C-C, 4) above the bond center C-N, 5) above the center of a hexagon (Figure 2).



Figure 2. A boron atom positions on the surface of the polymer monolayer.

We studied the process of a boron atom adsorption on the surface of a PPAN in hard scanning mode, namely, when scanning, we changed the distance between the selected boron atom and the monolayer of the polymer without optimizing the rest of the geometric parameters. We changed the bond length fifteen times with an increment of 0.1 A. In positions 1 and 2, the adsorbed boron atom was attached to a carbon or nitrogen atom that were located approximately in the middle of the polymer cluster, which allowed us to exclude edge effects. The selected boron atom approached the PPAN layer along the perpendicular drawn through the selected polymer atom to the surface. The performed calculations made it possible to construct profiles of the adsorption processes potential energy curves (Figure 3).

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Figure 3. Surface profiles of the adsorption processes potential energy curves in various positions (hard scanning).

An analysis of the energy curves showed that boron atoms are adsorbed on the surface of the PPAN, which is confirmed by the presence of a minimum on the energy curves. It should be noted that the adsorption process depends on the selected adsorption center. So, when adsorption takes place on a nitrogen atom, the boron atom needs to overcome the energy barrier Ea = 0.2 eV, equivalent to the activation energy. We calculated activation energy as the difference between the total energy E (R) of the PPAN - atom B system at a certain distance R and the sum of the total energies of a boron atom and the polymer (i.e., at a distance $R = \infty$): $Ea = E_{PPAN} + (E_{PPAN} + E_B)$.

Similarly, we simulated interaction processes for positions 3, 4, and 5 of atomic orientation above the surface of pyrolyzed polyacrylonitrile. The atom incrementally approached the fictitious atom located either above the C – C and C – N bond center, or above the center of a carbon hexagon. We compared the energy curves and defined that when a boron atom is located above the middle of the C – C bond, two energy minima are present on the curve, Along with chemical adsorption, physical adsorption of a boron atom is also observed. To form a bond, a boron atom must overcome an energy barrier of a E_a (activation energy). The main energy characteristics of the adsorption process are presented in table 1.

PPAN: E_{ad} adsorption energy, E_a -activation energy, K_{ad} -adsorption distance.						
№ position	E _{ad} , eV	E _a , eV	R _{ad} , Å			
1	-1.97	-	1.8			
2	-0.8	0.2	1.7			
3	-1.66	0.17	1.8			
4	-0.8	-	1.7			
5	-1.6	-	1.6			

Table 1. The main energy characteristics of a boron atom adsorption process on the monolayer PPAN: E_{ad} adsorption energy, E_{a} -activation energy, R_{an} -adsorption distance.

Next, we examined the optimized structure of a polymer with an adsorbed boron atom. We studied five positions for a boron atom above the surface of the PPAN layer, as they were described, at distances corresponding to the energy minimum (Table 1). We performed calculations with

optimization of all geometric parameters, and found that the adsorption of a boron atom breaks the planarity of the layer. An atom that becomes the active center of adsorption leaves its position as it moves towards the boron atom pulling adjacent atoms along with it and they also rise above the surface of the PPAN. An increase by about 5 -7%. in the bond lengths of the nearest neighbors of the adsorption center is observed. The process of adsorption of a boron atom in the middle of the C - C or C - N bond takes place in a similar manner: in these cases, two atoms of the PPAN monolayer leave the initial position and rise above the surface.

An analysis of the geometry characteristics for the position where the adsorbed atom is located above the center of the hexagon of the layer (position 5) showed that the boron atom, when it is at a distance of 1.6 Å from the surface of the PPAN, begins to shift from the center of the hexagon to the nitrogen atom, while the nitrogen atom drops down, the bond C-N lengthens, and adjacent carbon atoms rise above the layer and form a bond with the boron atom. As a result of calculations performed with full optimization of the parameters, the spatial configuration of the structure, the bond lengths, local charges (q) and binding energy (Esb) were established for the PPAN + boron atom adsorption complexes for various positions of atoms above the surface (table 2). The binding energy was calculated by the formula

$$\mathrm{E}sb = \frac{\mathrm{E}tot - Nc\mathrm{E}c - N_{N}\mathrm{E}_{N} - N_{H}\mathrm{E}_{H} - N_{B}\mathrm{E}_{B}}{N},$$

where N is the total number of atoms in the structure; Etot is the total energy of the structure; Nc is the number of carbon atoms; Ec is the energy of a carbon atom; N_N is the number of nitrogen atoms; E_N – energy of a nitrogen atom; $N_{\rm H}$ is the number of hydrogen atoms; $E_{\rm H}$ is the energy of a hydrogen atom; N_B is the number of boron atoms; E_B is the energy of a boron atom.

An analysis of the electronic energy structure of the PPAN + boron atom nanosystems found that the orbital levels are combined into groups that can be considered analogs of the valence and conduction bands of the crystal. The energy difference between the upper occupied and lower vacant molecular orbitals can be interpreted as the band gap ΔEg . The results of calculating the energies of the boundary orbitals of E_{HOMO} and E_{LUMO} , the band gap ΔEg for all adsorption complexes obtained by adsorption of a boron atom on the plane of pyrolyzed polyacrylonitrile are presented in Table 3. Comparison of the band gap of the obtained complexes "PPAN + boron atom" with the same characteristic of pure PPAN found that in all implemented adsorption positions, an increase in ΔEg occurs, i.e. the attachment of a boron atom to the surface of the PAN causes a change in the type of conductivity of the resulting composite, which can be experimentally fixed and, accordingly, used to create nanoelectronic devices.

	Table 2. The main geometry paremetres of the adsorption complex PPAN+a boron atom.						
N⁰	The structure with the optimized geometry	Bond	Charges on	Bond			
posit		lenght, Å	atoms	energy,			
ion				eV			
1		R _{B-C} =1.67	Q _B =0.561	7.52			
	A 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	$R_{C-C}=1.48$	Qc=-0.339				
	T						
1		R _{B-C} =1.67 R _{C-C} =1.48	Q _B =0.561 Q _C =-0.339	7.52			

. C (1



Table 3. Electronic and energetic characteristics of PPAN-based composite with a boron atom: E_{HOMO} – energy of highest occupied molecular orbital, E_{LUMO} - energy of lowest vacant molecular orbital; ΔEg – a band gap.

Position number	E _{HOMO} , eV	E _{LUMO} , eV	ΔE_{g} , eV
PPAN	7.01	2.82	4.19
1	8.31	1.82	6.49
2	7.03	2.75	4.28
3	8.24	2.6	5.64
4	8.11	2.2	5.91
5	7.87	2.32	5.55

5. Introduction of a boron atom into the polymer matrix

Next, we simulated and examined the process of a boron atom introduction into the PPAN monolayer. We simulated the process by incremental approach of a boron atom to the polymer layer, which contained a vacancy (the so-called V-defect). This made it possible to construct a surface profile of the potential energy of the system "PPAN - atom B". An analysis of the calculation results showed that the atom approached the vacancy center barrier free and formed a bond with carbon atoms of the polymer. The B – C bond length was found to be 1.5 Å, while the lengths of adjacent C – C bonds depleted to

1.3 Å. Figure 4 shows the structure of $C_{43}N_{14}BH_{10}$. The results of the calculation of this structure are presented in table 4.



Figure 4. Simulation of a boron atom introduction into the monolayer of PPAN.

6. A study of multiple adsorption of a boron atom on the monolayer of PPAN

We also investigated the possibility of boron atoms multiple adsorption on the surface of the PPAN polymer. In the vicinity of a boron atom, a second boron atom was attached to the monolayer, then a third one was placed next to the two atoms and, finally, a fourth one was introduced. The spatial geometry of the obtained structures is shown in Figure 5. The calculation results of the main characteristics of these processes are presented in table 4.

We have found that when multiple adsorption of boron atoms on the surface of a PPAN takes place monolayer the binding energy decreases and planarity of the system breaks, thereby twisted PPAN structures form. We studied the dynamics of the band gap and found that an increase in the number of boron atoms on the polymer surface results in an increase in ΔEg .



Figure 5. The structure after the parametres were optimized of pyrolyzed polyacrylonitrile modified by boron atoms: a) $C_{44}N_{14}H_{10}B_2$; b) $C_{44}N_{14}H_{10}B_3$; c) $C_{44}N_{14}H_{10}B_4$.

Structure	E _{HOMO} ,	E _{LUMO} ,	$\Delta \mathbf{E}_{\mathbf{g}},$	Charges on	Max	Min	Bond
	eV	eV	э٧	a boron	charge	charge	energy,
				atom			eV
C44N14H10	7.01	2.82	4.19	-	0.55 on a	-0.393 on a	7.91
					nitrogen	carbon atom	
					atom		
C ₄₃ N ₁₄ BH ₁₀	8.37	2.22	6.15	0.464	0.464 on a	-0.219 on a	7.93
					boron atom	carbon atom	
$C_{44}N_{14}H_{10}B_2$	7.3	3.07	4.23	Q _{B1} =-0.294	0.653 on a	-0.457 on a	7.51
				Q_{B2} =-0.173	nitrogen	carbon atom	
					atom		
$C_{44}N_{14}H_{10}B_3$	8.32	2.6	5.72	Q_{B1} =-0.221	0.703 on a	-0.429 on a	7.47
				Q_{B2} =-0.429	nitrogen	boron atom	
				$Q_{B3}=0.584$	atom		
$C_{44}N_{14}H_{10}B_4$	7.69	2.59	5.1	$Q_{B1}=0.018$	0.346 on a	-0.296 on a	7.43
				$Q_{B2}=0.006$	nitrogen	carbon atom	
				$Q_{B3}=0.280$	atom		
				Q_{B4} =-0.261			

Table 4. The main characteristics of pyrolyzed polyacrylonitrile doped with boron atoms.

7. Conclusion

So, the performed studies have shown that a boron atom is adsorbed on the surface of the PPAN, while a carbon atom is the most advantageous active adsorption center. The calculations made it possible to establish the fact of a boron atom introduction into the structure of a monolayer. The study of multiple adsorption of boron atoms have shown that polymer modification leads to a change in the conductivity of the system, which is illustrated by an increase in the band gap of the obtained composite. Thus, we can conclude that on the basis of PPAN, it is possible to obtain a new material saturated with boron atoms, which can act as an amorphizing element, enabling the creation of a metal composite material based on pyrodized polyacrylonitrile with metal compounds in an amorphous state. This will allow to obtain new nanomaterials with unique characteristics that can be used in telecommunications systems, in solar generators, electromagnetic screens as new radar absorbing materials, and so on.

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