Physicochemical properties of polymer-polymer nanocomposites based on polyaniline and water-soluble vinyl polymers

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Polymer-polymer composites (PPC) derivate of polyaniline and water-soluble vinyl polymers have unique physical and chemical properties. Along with good forming properties these PPC have electrical conductivity which makes them perspective platforms for designing various sensors devices [1, 2]. In this paper, we received and studied the physicochemical properties of PPC, derived from polyvinyl alcohol (PVA) and polymethacrylic acid (PMA) and polyaniline (PANI). Composites with different content of components were obtained by the mechanic-chemical method, mixing in a small amount of water PVA or PMA with PANI.

An important characteristic of PPC is thermo-mechanical properties. The thermo-mechanical curve of PVA has a classical character (**Figure 1**). As the PANI content increases, the composite becomes elastic at lower glass transition temperatures (**Figure 2**), which indicates the interaction of macromolecules of different natures in the polymer matrix. The dependence of the transition temperature of PPC from glassy to highly elastic state on the content of polyaniline is shown in **Figure 3**.

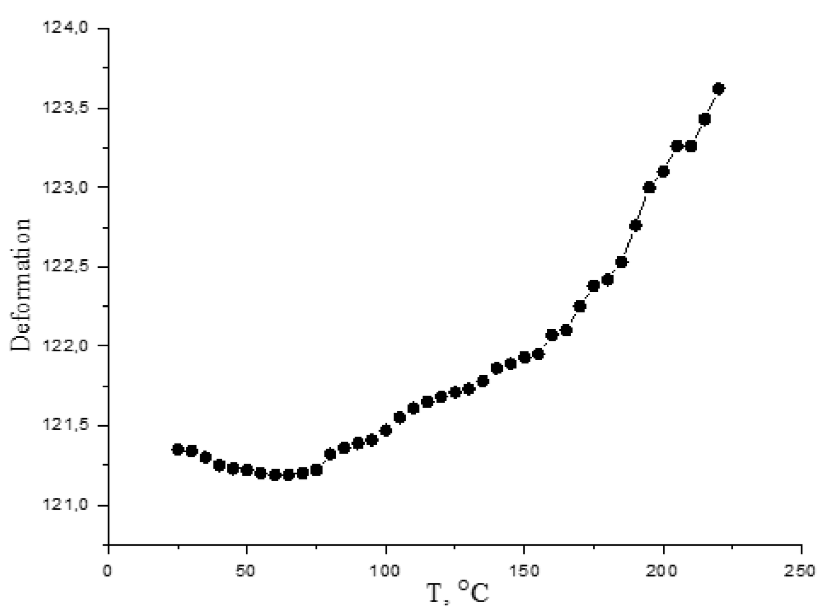


Figure 1. Thermo-mechanical curve of polyvinyl alcohol

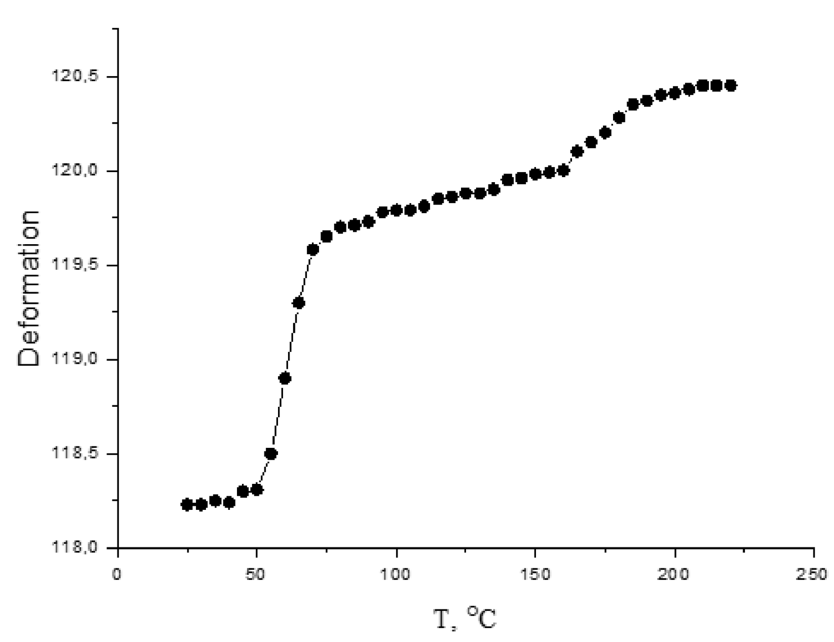


Figure 2. Thermo-mechanical curve of a composite of polyvinyl alcohol and polyaniline 5%

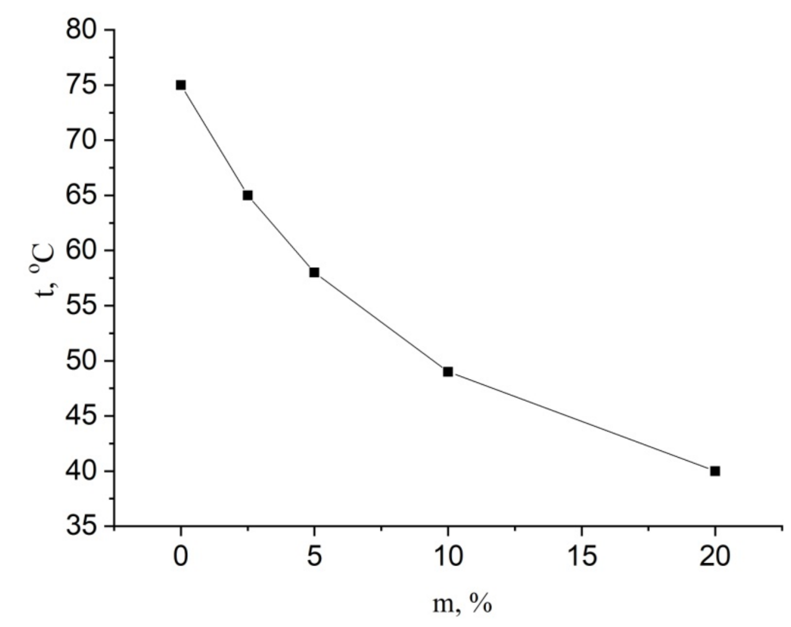


Figure 3. Dependence of temperature of transition from glassy state to high-elasticity on the PANI content (m, %)

An important characteristic of PPC is their electrical conductivity. The results of the study of the electrical conductivity of composites based on polyaniline and polyvinyl alcohol are presented in **Table**. As expected, an increase in the PANI content in the composite leads to a significant increase in electrical conductivity.

Table. The dependence of resistance and electrical conductivity of polymer-polymer composites on the content of PANI

Contents PANI (%)	l (mm)	R (Om)	ρ (Om·cm)	σ (Sm/cm^{-1})
2	11.1	51400	38000	$2.63\cdot10^{-5}$
5	7.25	16800	19000	$5.26\cdot10^{-5}$
10	8.50	18900	18200	$5.48\cdot10^{-5}$
20	8.90	67.8	62.5	$1.60\cdot10^{-2}$
40	9.50	7.75	6.69	$1.49\cdot10^{-1}$
70	7.10	1.17	1.35	$7.41\cdot10^{-1}$

The temperature dependence of the electrical conductivity of a composite containing 70% polyaniline and 30% PVA is shown in **Figure 4**. An increase in temperature leads to an increase in electrical conductivity. According to the tangent of the angle of inclination, the activation energy of electrical conductivity (ε_σ) was calculated, which is 0.128 eV. For a composite containing 40% PANI and 60% PVA, the numerical value ε_σ is close to a composite consisting of 70% PANI and 30% PVA and equal to 0.156 eV.

The determined parameters of charge transfer indicate that the composites based on PANI and PVA are typical organic semiconductors. The activation energy of charge transfer, which is approximately half the width of the bandgap of the semiconductor, does not exceed 0.32 eV, indicating a low energy barrier for these composites.

X-ray studies by powder diffraction [3] confirm the conclusions about the interaction between the macromolecules of PANI and PVA (**Figure 5**). For X-ray examinations, powder samples were prepared from the original samples by thorough grinding in an agate mortar. The sample powder was applied in a uniform layer on a special film for X-ray experiments on the passage and fixed with a second film in the cell on the passage.

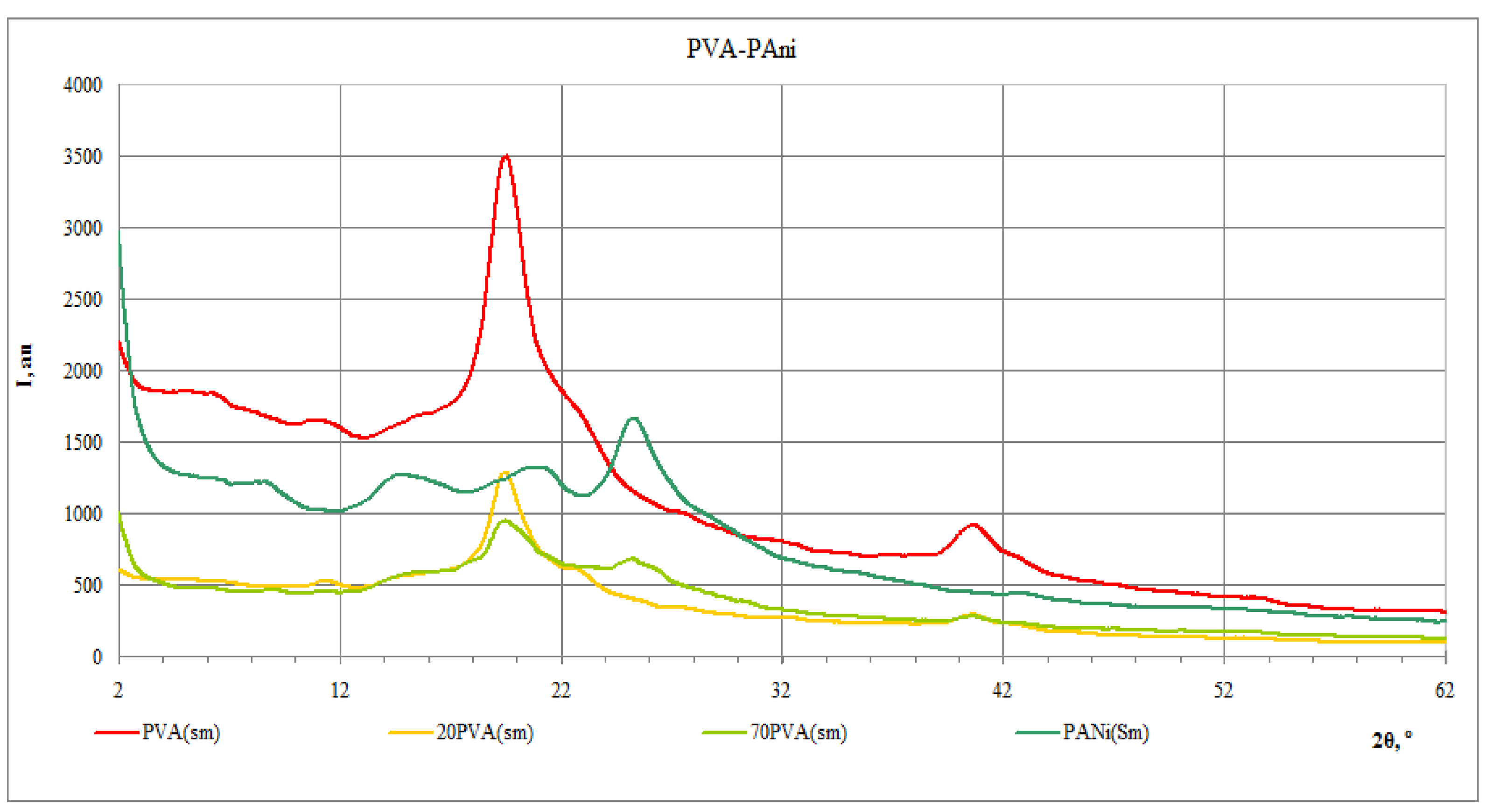


Figure 5. XRD pattern of PVA, PANI, PPC with 20% PVA and 70% PVA

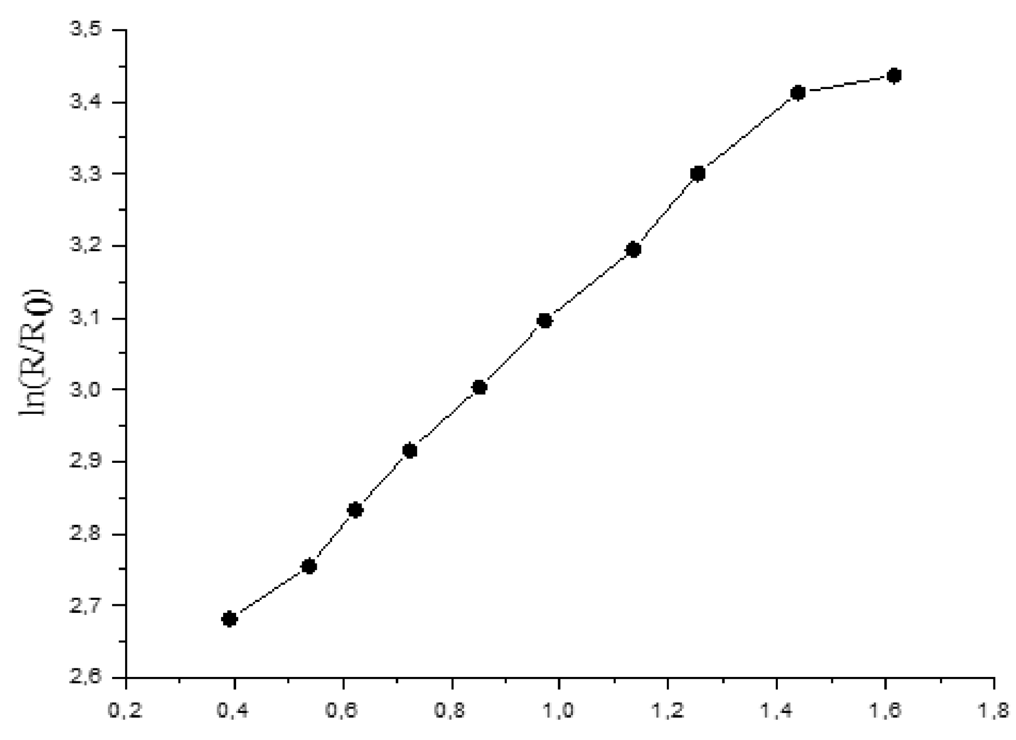
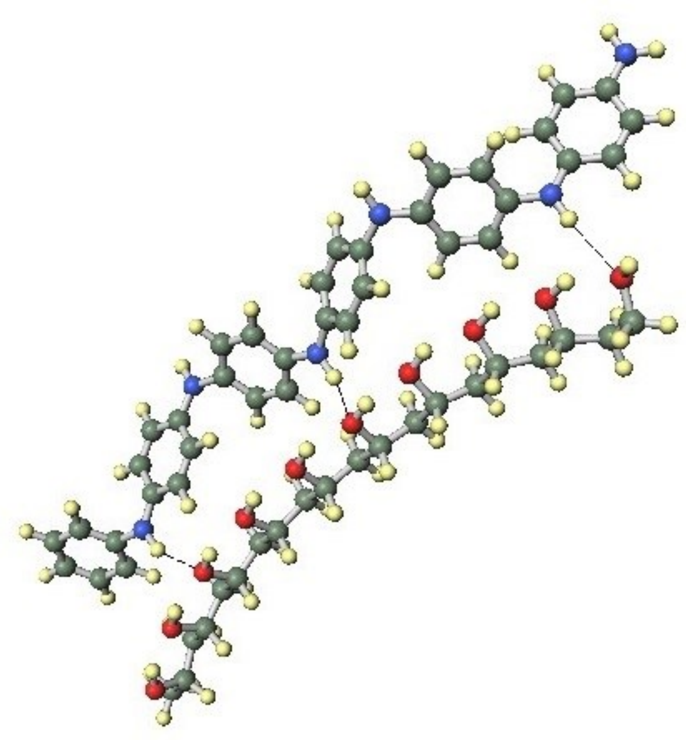


Figure 4. Dependence of conductivity of composite based on PVA (30%) and PANI (70%) on temperature

Quantum–chemical calculations of PPCs based on PVA and PANI were carried out using the semiempirical program MOPAC2016 [4] with the graphical interface Winmostar [5]. We used different semiempirical methods to optimize the geometric structure and calculate the heat of formation ($\Delta_f H^{298}$) and energies of the highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals, as well as charges on atoms by Mulliken.

The obtained results indicate that a strong intermolecular interaction is realized between the macromolecules of PANI and PVA due to the formation of hydrogen bonds between the hydrogen atoms of PANI and the oxygen atoms of PVA (**Figure 6**). Calculations of partial charges on oxygen, nitrogen, and related hydrogen atoms confirm this conclusion.

Figure 6. Formation of hydrogen bonds between hydrogen atoms of PANI and oxygen atoms of PVA



Also, the calculation of thermodynamic parameters (enthalpy, entropy, and heat capacity) of individual PANI and PVA macromolecules and their comparison with the thermodynamics of the PANI-PVA intermolecular complex also indicates a strong interaction between polymers.

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