In the temperature range of 25–70 °C, the complexation process of PVA with Cu^{2+} ion is accompanied by the release of heat (exothermic process), as a result of which the strength and stability of the polymer-metal complex decreases with temperature increasing.

Thus, based on analysis of the results of potentiometric and conductometric analysis, the formation of copper(II)-PVA polymer complex and its composition were established.

3.5. IR spectroscopy and SEM studies

The process of the formation of the copper(II)-PVA complex is characterized by the negative value of the change in entropy, which is caused by the existence of donor-acceptor bond in the studied complex. This also indicates that the ratio between copper(II) ion and PVA is 1:2. To study the surface of the pure polymer and the polymer-metal complex, the scanning electron microscopy (SEM) method was used; the results of the study are presented in Figures 4 and 5. A comparison of microscopic images of the pure polymer and the resulting complex indicates the formation of porous spherulites of different sizes.

The infrared spectrum was acquired for polyvinyl alcohol and the complex copper(II) acetate – PVA (Figure 6).

Table 1 Values of Bjerrum's formation functions of the $Cu(OAc)_2$ – PVA complex at 70 °C and I =0.01 mol/L.

$[LH^+]\cdot10^4$ (mol L^{-1})[a]	pL[b]	$L\cdot10^6$ (mol L^{-1})[c]	$L_c\cdot10^3$ (mol L^{-1})[d]	n[e]
3.33	5.39	4.12	3.00	2.00
6.66	6.04	0.922	2.67	1.78
9.99	6.33	0.462	2.33	1.56
13.30	6.69	0.206	2.00	1.33
16.60	6.83	0.149	1.67	1.11
20.00	7.22	0.0597	1.34	0.89
23.30	9.42	0.000381	1.00	0.67
26.60	10.67	0.0000213	0.67	0.45
30.00	12.29	0.000000517	0.34	0.23
33.3	13.91	0.0000000124	0.014	0.01

[a] $[LH^+]$ – concentration of the protonated ligand groups;
[b] pL or $-\lg[L]$ – concentration of the free ligands calculated on Henserson-Hasselbach equation $pH = pK\alpha + m\lg[L]/[LH^+]$, where m – the empirical coefficient considering interlink interaction of a polymeric chain;
[c] $[L]$ – concentration of the free ligands which are not involved in a complexing process;
[d] $[L]_C$ – concentration of the ligand groups connected in a complex;
[e] n – Bjerrum's formation functions or average coordination number of a metal ion.

Table 2 Thermodynamic characteristics of the complexation.

T, °C	$-\Delta_rG^o$, kJ/mmol[a]	$-\Delta_rH^o$, kJ/mmol[b]	$-\Delta_rS^o$, kJ/mmol·K[c]
25	0.32	1.6328	0.004405
45	0.23	1.0900	0.002704
70	0.16	1.3502	0.003470

[a] Δ_rG^o – Gibbs's energy change of reaction;
[b] Δ_rH^o – enthalpy change of reaction (heat effect);
[c] Δ_rS^o – entropy change of reaction.

By comparing these two IR spectra, a displacement of the band position ν_{O-H} is clearly seen. In the polyvinyl alcohol infrared spectrum, the position of ν_{O-H} changes from 2390 to 2410 upon complexation with Cu(II), which can be seen in the infrared spectrum of the complex based on copper(II) acetate – polyvinyl alcohol, indicating its participation in the formation of copper – polymer complex [20]. It gives strong indication of specific interactions between the ligand and metal ion.

3.6. Oxidation of yellow phosphorus (P4) catalyzed by $Cu(PVA)_2(OAc)_2$ complex under mild conditions

The synthesized catalyst was used in the process of oxidation of phosphorus at room temperature in the presence of oxygen at atmospheric pressure:

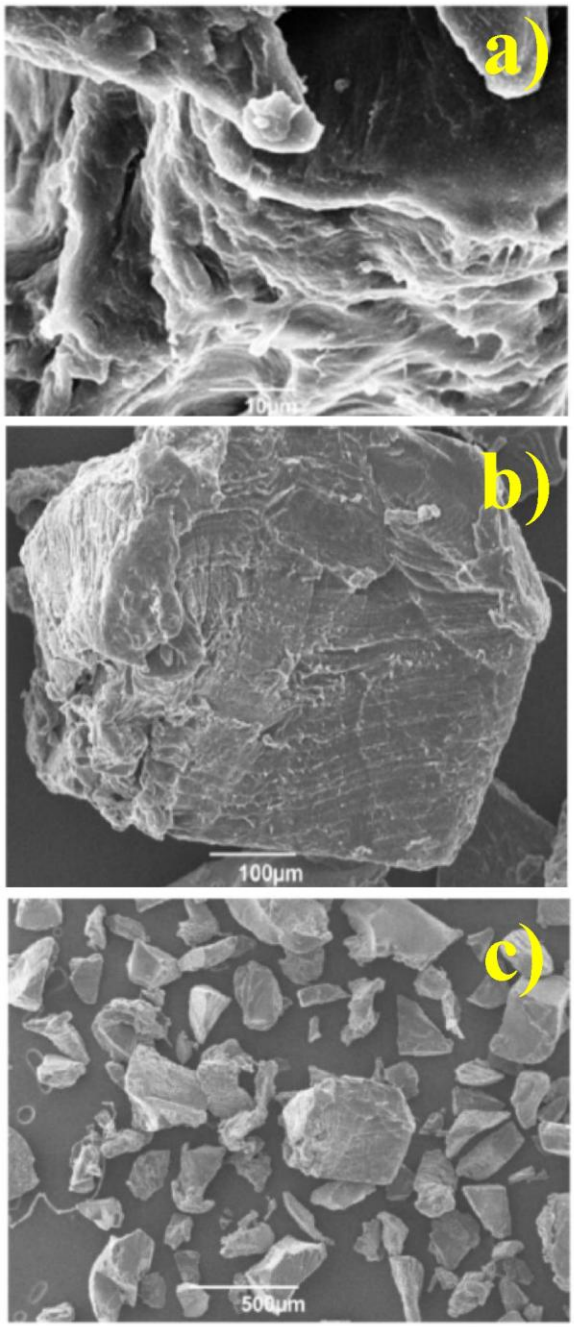

Figure 4 SEM micrographs of polyvinyl alcohol.