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Polymer–metal complexes based on gellan

Summary — By dropwise adding solutions of gellan (Gll) or gellan + poly(vinyl alcohol) (PVAL) mixture into different metal salt solutions — $FeCl_3 \cdot 6\ H_2O$, $FeCl_2 \cdot 4\ H_2O$, $CoCl_2 \cdot 6\ H_2O$, $CuCl_2 \cdot 2\ H_2O$ — at 30 °C under constant stirring, preparation of spherical microparticles based on polymer-metal complexes has been performed. FT-IR spectroscopy, TGA analysis and swelling measurements of these microparticles in water showed the influence of the metal type ions on their structure, thermal stability and water swelling capacity. The FT-IR spectroscopy allows to explain the mechanism of polymer-metal complexes formation and the optical microscopy showed that the microparticles obtained had good sphericity with average diameter ranging from 719 μm to 830 μm. The thermal stability of the polymer-metal complexes was found to be higher than that of the gellan.

Keywords: gellan, poly(vinyl alcohol), metal-polymer complexes, ionotropic gelation, thermal stability, swelling in water.

KOMPLEKSY POLIMER-METAL NA PODSTAWIE GELANU

Streszczenie — Opisano prosty i łatwy do zrealizowania sposób otrzymania w temp. 30 °C kompleksów gelanu (Gll — anionowy, wielkocząsteczkowy, dezaktywowany polisacharyd pochodzenia naturalnego) lub mieszanin Gll + poli(alkohol winylowy) (PVAL) z wodzianami różnych soli metali ($FeCl_3$, $FeCl_2$, $CuCl_2$, $CoCl_2$) (rys. 1, tabela 1). Kompleksy mają postać regularnych okrągłych mikrocząstek o wymiarach 719—830 μm. Na podstawie widm IR (rys. 2 i 3, tabela 2) zinterpretowano mechanizm powstawania kompleksów i określono ich budowę. Zbadano termostabilność kompleksów oraz kinetykę ich degradacji cieplnej (rys. 4, tabela 3); jest to wieloetapowy proces o skomplikowanym przebiegu. Scharakteryzowano zjawisko pęcznienia kompleksów w wodzie w temp. 25 °C (rys. 5, tabela 4) ustalając następującą zależność stopnia spęcznienia od rodzaju zawartego w nich metalu: $Fe^{3+} < Fe^{2+} < Cu^{2+} < Co^{2+}$.

Słowa kluczowe: gelan, poli(alkohol winylowy), kompleksy metal-polimer, żelowanie jonotropowe, termostabilność, pęcznienie w wodzie.

Polymeric materials with the ability to create complexes with metal ions are very common, originating from both natural and synthetic sources [1—3]. Recent progress made in design and synthesis of novel coordination polymers has brought a variety of polymeric materials that exhibit the structural diversities and attractive properties which can be further utilized in various fields, like catalysis [4, 5], sewage treatment [6], optics, luminescence and sensor technology [7] or polymer drug grafts [8, 9]. A polymer-metal complex is a coordination complex between a ligand functional group anchored to a polymer matrix and a metal ion, in which the metal ion is attached to the polymeric ligand by a coordinate bond. The synthesis of a polymer-metal complex can take place by the synthesis of a macromolecular ligand followed by the binding of the metal salts which involves different processes, such as complexation, coordination, ion exchange and electrostatic attraction or by the incorporation of a metal by polymerization of a suitable metal containing monomer [10]. With repetitive functional groups, biopolymers are excellent chelating and complexing materials for a wide variety of applications, especially in medicine and pharmaceutical industry.

Among them, gellan gum (Gll) is an anionic high molecular weight, deacetylated exocellular polysaccharide produced as a fermentation product by a pure culture of a gram negative bacterium, namely *Pseudomonas elodea* [11], with a tetrasaccharide repeating unit of one α-L-rhamnose, one β-D-glucuronic acid and two β-D-glucose residues.

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The first investigation on the metal complexes of gellan has been done few years ago. It is well known that gellan gum forms gels in the presence of mono- and divalent cations due to the screening of the electrostatic repulsion between the carboxylate groups in the gellan gum chains (case of monovalent cations) or *via* ionic crosslinking between divalent cations and two carboxylate groups belonging to the glucuronic acid molecules from the gellan chains in addition to the screening effect (case of the divalent cations) [12]. Thus, in the recent years many publications were focused on the rheological studies [13, 14] as well as the investigation on the conformational changes of gellan in the solutions containing mono- and divalent cations. Different experimental techniques such as ^{1}H NMR, circular dichroism and diffusion measurements, were used in these works [15]. Also, the crosslinking reactions, leading to hydrogels, have been already investigated on this polysaccharide [16, 17].

Taking into account the fact that some minerals, *i.e.* iron, cobalt or copper in appropriate amounts are essential nutrients for the human health, the present study has the aim to synthesize new microparticles based on the polymer-metal complexes which could be used as materials for controlled delivery of drugs or dietary supplements. Thus, the paper informs about the synthesis and characterization of the microparticles based on gellan and a mixture of gellan — poly(vinyl alcohol) (PVAL)-metal complexes using a simple and economic method, namely ionotropic gelation.

EXPERIMENTAL

Materials

Deacetylated gellan gum ($\overline{M}_w$ = 500.000 g/mol), PVAL (degree of hydrolysis 88 %, $\overline{M}_w$ = 50.000 g/mol), iron(III) chloride hexahydrate ($FeCl_3 \cdot 6\ H_2O$), iron(II) chloride tetrahydrate ($FeCl_2 \cdot 4\ H_2O$), copper(II) chloride dihydrate ($CuCl_2 \cdot 2\ H_2O$) and cobalt(II) chloride hexahydrate ($CoCl_2 \cdot 6\ H_2O$) were purchased from Fluka Company. All the substances have been used without further purifications. Bidistilled water was used in all experiments.

Preparation of microparticles based on polymer-metal complex

Complex microparticles were prepared *via* ionotropic gelation method [18]. Gellan gum with PVAL (molar ratio Gll:PVAL = 1:1) or without PVAL was dissolved in bidistilled water and the solutions with concentration of 1 % (w/v) were prepared. Then polymer solutions were added dropwise into gelation media of 0.1 equiv · L^{-1} metal salt concentration at 30 °C, using a 20 ml hypodermic syringe equipped with a needle 12 mm in length and 0.45 mm in diameter. In order to obtain perfectly spherical particles the optimum stirring speed was 200 rpm. The pH of gelation media was 2.81—4.86. The beads with good sphericity thus formed were cured in the gelation medium for 24 h, centrifuged followed by washed in distilled water and finally dried under vacuum conditions at room temperature. All the reaction parameters, namely distance between the syringe and gelation media (12 cm), the speed of stirring and the temperature, were maintained constant during all experiments. Schematic representation of the ionotropic gelation method is shown in Figure 1.

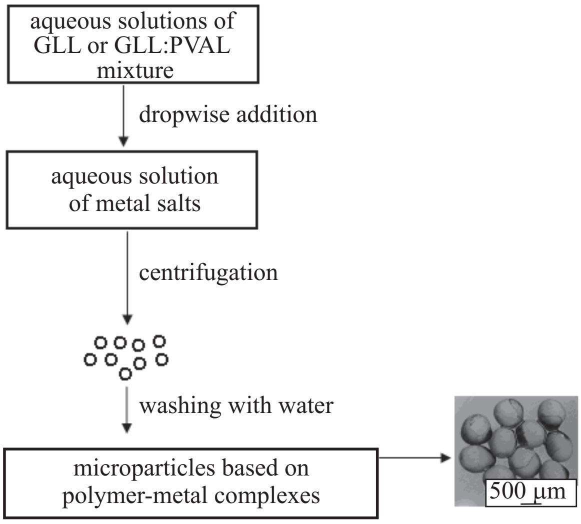


Fig. 1. Schematic representation of the ionotropic gelation method

Methods of microparticles characterization

— FT-IR spectra were recorded in the range between 4000 and 400 cm^{-1} on the Bruker Vertex 7.0 Fourier transform infrared spectrometer. Samples were prepared by dispersing the compounds in KBr and compressing the mixture to form a disc.

— Thermogravimetry (TGA) measurements were performed in a Mettler 851 Derivatograph, using a 4 mg sample and heated at a rate of 10 °C/min under nitrogen atmosphere. The weight losses *versus* temperature were recorded.

— The stereomicroscope (Alpha STO 5) was used to determine the shape and average diameter of microparticles. Also, the dried microparticles were sprinkled onto a glass plate, examined and the image was taken with a camera attached to the microscope.

— To determine the swelling degree of the microparticles based on the polymer-metal complexes the gravimetric method was used. Known amounts of dry beads (250 mg) were placed in the stainless steel cylinders with sieves, in the distilled water at 25 °C for a required period of time for the range between 10 min and 24 h. The swollen microparticles were centrifuged at 2000 rpm for 10 min and then weighed immediately on an electronic balance to determine the wet weight. The swelling degree (S_w) for each sample at time t was calculated using the following equation:

$$S_w(\%) = \frac{W_t - W_0}{W_0} \cdot 100 \qquad (1)$$

where: W_t *and* W_0 *— the weights of the complex microparticles at time t and the dry state, respectively.*

Average of three trials was taken.

Peppas method [19] was applied in order to characterize the kinetics of the swelling process of polymer-metal complexes, and therefore, the following equation was used:

$$\frac{M_t}{M_\infty} = k \cdot t^{n_d} \qquad (2)$$

where: M_t *— the mass of water uptake at time t,* M_∞ *— the mass of water uptake as time approaches infinity,* n_d *— diffusion exponent, characteristic for the transport mechanism, k — a constant.*

RESULTS AND DISCUSSION

Formation mechanism of complexes

When an aqueous gellan solution with or without poly(vinyl alcohol) was added to metal ion solution the spherical microparticles were instanly formed. The average diameter of the dried beads (resulting from the measurement of 20 beads) was evaluated using the optical microscopy (Table 1).

Table 1. Experimental conditions for preparation of the microparticles based on polymer-metal complexes at 30 °C*)

Sample code	Gll wt. %	Gll:PVAL molar ratio	Metal salts $MX_n \cdot nH_2O$	Color	D_{med} μm
1a	1	—	$FeCl_3 \cdot 6\ H_2O$	dark brown	743
1b	—	1:1	$FeCl_3 \cdot 6\ H_2O$	dark brown	719
2a	1	—	$FeCl_2 \cdot 4\ H_2O$	brown	790
2b	—	1:1	$FeCl_2 \cdot 4\ H_2O$	brown	772
3a	1	—	$CuCl_2 \cdot 2\ H_2O$	green	810
3b	—	1:1	$CuCl_2 \cdot 2\ H_2O$	green	780
4a	1	—	$CoCl_2 \cdot 6\ H_2O$	mauve	830
4b	—	1:1	$CoCl_2 \cdot 6\ H_2O$	mauve	815

*) 1a—4a represent the microparticles based on the gellan; 1b—4b are the microparticles based on the gellan + PVAL mixture.

The steady-state condition was assumed as migration of a number of Na^+ ions produced by the dissociation of sodium carboxylate groups belonging to the gellan chains. This number of ions migrated from the microparticle to the electrolyte solutions, whereas the metal ions moved in the opposite direction and took the free places left by Na^+ ions. Also, the metal ions coordinate the donor atoms from functional groups of the gellan chains and therefore, the bridges of carboxylate and/or hydroxyl groups have been formed. The stoichiometry of such gelation processes can be expressed by the following chemical reaction (3) [20].

$$\mathrm{m(Gll{-}COO^-Na^+)_n + n\ M^{m+}} \rightarrow$$
$$\rightarrow \mathrm{[(Gll{-}COO^-)_m M^{m+}]_n + m{\cdot}n\ Na^+} \qquad (3)$$

An additional proof of the formation mechanism for the polymer-metal complexes is illustrated by FT-IR spectra of the polymer support and its complexes (Figures 2 and 3).

In the case of Gll, the following characteristic peaks are observed: -OH stretch vibration of hydroxyl groups at 3422 cm^{-1}, >CH- stretch vibration of methylene groups at 2920 cm^{-1}, asymmetric carboxylate anion stretching at 1611 cm^{-1}, symmetric carboxylate anion stretching at 1415 cm^{-1} and primary -OH groups stretching at 1029 cm^{-1}. The FT-IR spectrum of Gll was compared to spectra of Gll-metal complexes. These latter spectra exhibit many differences, namely:

— The wide band at 3422 cm^{-1} corresponding to the stretching vibration of -OH groups in gellan shifted to higher frequencies for metal complexes as follows: 3437 and 3436 cm^{-1} for 1a and 1b, respectively, 3435 and 3436 cm^{-1} for 2a and 2b, 3437 and 3435 cm^{-1} for 3a and 3b as well as 3439 and 3436 cm^{-1} for 4a and 4b, indicating the involvement of hydroxyl groups in the complexation with the metal ions.

— The peaks at 2923 cm^{-1} and 2854 cm^{-1} are attributed to the asymmetrical and symmetrical >CH- stretching of the $-CH_3$ and methylene groups.

— The appearance of the absorption band at approximately 1735 cm^{-1}, which corresponds to the carboxyl groups, indicates that some carboxylate groups of the gellan are transformed in the carboxylic groups during the treatment with the metal salts solution at acidic pH (pH = 2.81—4.68).

— The absorption band of the asymmetric and symmetric stretching vibration of >C=O of carboxylate groups shifted to higher wave number, as well as the appearance of the absorption bands between 1543—1580 cm^{-1} in the complexes spectra, indicating involvement of the carboxylate groups in the coordination process. It is well known that the difference Δ value between the asymmetric and symmetric stretching frequencies [$\nu_{as}(COO^-)$ and $\nu_s(COO^-)$] can reflect the coordination modes of the carboxylate group [21]. From Table 2 it can be observed that the values of Δ between 164 and 175 cm^{-1} correspond to the chelating mode.

— In all spectra the band at 1029 cm^{-1} corresponding to the stretching vibration of the primary -OH group disappeared (see Fig. 2, Gll) and a new band appears to a higher wave number (1038—1042 cm^{-1}). This result suggests that -OH groups are involved in the coordination with metal ions. All of these observations allowed us to propose the possible schematic configurations of the polymer-metal complexes (Scheme A).

Thermodegradation

Thermogravimetric studies on the polymer-metal complexes reveal the changes of thermal stability of the

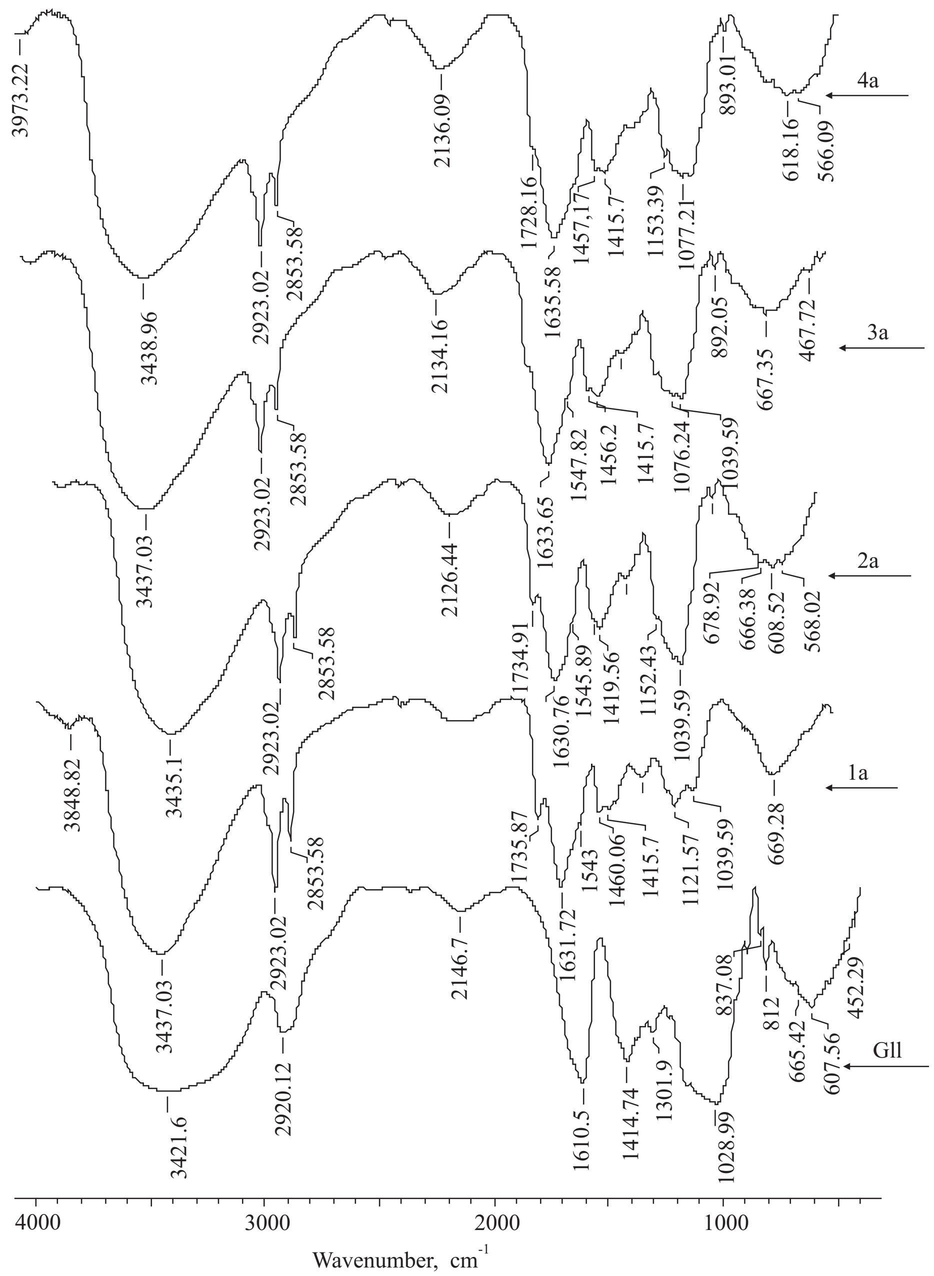


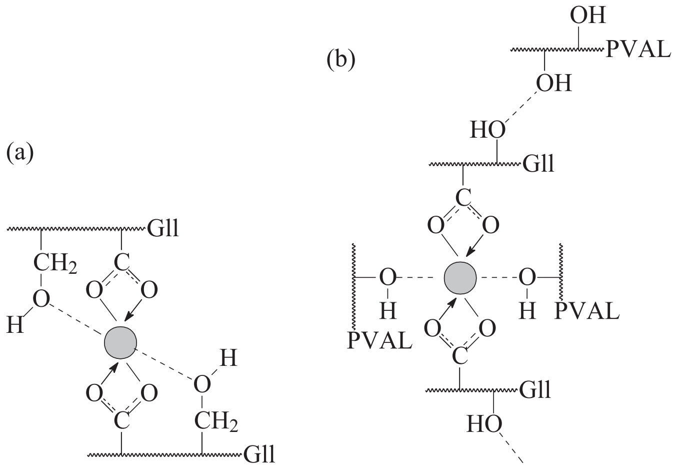
Fig. 2. FT-IR spectra of the microparticles based on Gll-metal complexes (Table 1, samples 1a—4a)

Table 2. Infrared data of the microparticles based on the polymer-metal complexes

Sample code (see Table 1)	$\nu_{asym(COO^-)}$, cm^{-1}*)	$\nu_{sym(COO^-)}$, cm^{-1}	Δ**), cm^{-1}
1a	1632, 1543	1416	172
1b	1632, 1580, 1543	1421	164
2a	1631, 1546	1420	169
2b	1632, 1546	1424	165
3a	1636, 1545	1416	175
3b	1634, 1545	1417	173
4a	1634, 1548	1416	175
4b	1633, 1548	1416	174

*) For Δ estimation an average value was considered.

**) $\Delta = \nu_{asym(COO^-)} - \nu_{sym(COO^-)}$.



Scheme A. Possible structures of the gellan-metal complexes (a) and gellan + PVAL mixture-metal complexes (b); ● — metal ions

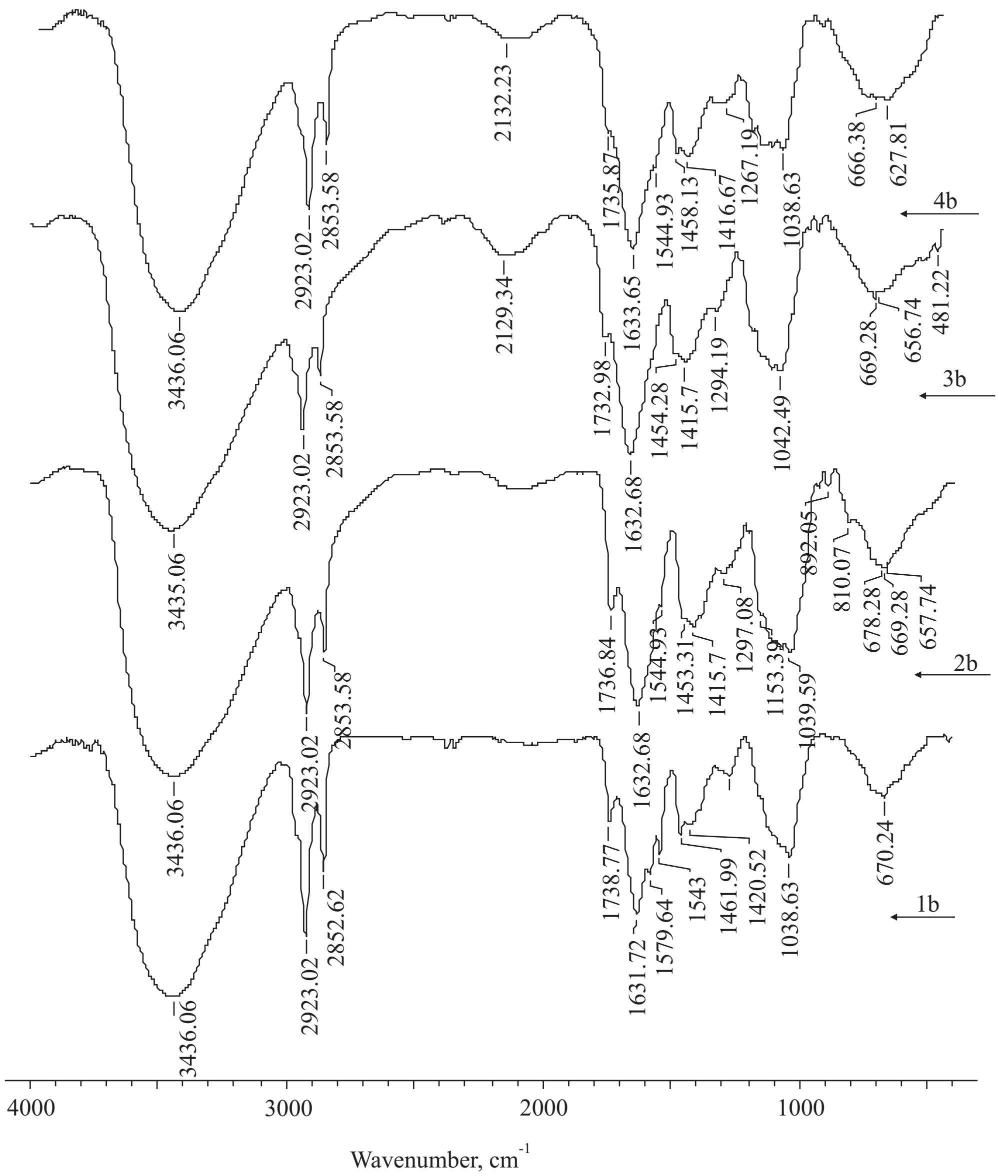


Fig. 3. FT-IR spectra of the microparticles based on Gll + PVAL mixture-metal complexes (Table 1, samples 1b—4b)

polymer on the metal complexation. The thermogravimetric analysis data and the TGA thermograms are shown in Table 3 and Figure 4, respectively.

The thermogravimetric analysis for both started polymers (Gll and PVAL) is well known from literature [22, 23], namely TGA of Gll revealed two stages of decomposition, while of PVAL revealed three stages of decomposition. As can be seen from Fig. 4, polymer-metal complexes 1a and 1b undergo four stages of decomposition, 3a and 3b undergo two stages of decomposition, whereas 4a and 4b undergo three stages of decomposition. In the first stage (60—170 °C) the weight loss might be due to the removal of the coordinated water molecules. After most of the hydrogen bonds are broken, the main degradation process of the microparticles based on the polymer-metal complexes occurs in the second stage of decomposition.

As it can be seen from Table 3, the metal complexes with PVAL [(b) samples] are found to have higher thermal stability than the metal complexes without PVAL [(a) samples] because the presence of the PVAL inside the microparticles led to a more stable network with a complex structure compared with those based on gellan only.

Kinetic parameters, such as energy of activation and reaction order calculated with the Coats-Redfern [24], Flynn-Wall [25] and Urbanovici-Segal [26] methods are also summarized in Table 3. The results show that the values obtained with various methods are comparable. Values of fractional reaction order ranged between 1.5 and 2 indicating the complexity of the degradation process of all microparticle types.

Water swelling

The water swelling capacity is an important property of the microparticles based on the polymer-metal complexes and was also investigated in the present study. This characteristics was determined by swelling of the

Table 3. TGA results and kinetic parameters for the metal complex microparticles*)

Sample code (see Table 1)	Decomposition temperature, °C		Weight loss %	E_a, kJ/mol			n
	T_i	T_f		C-R	F-W	U-S	
1a	67	149	13.18	50.22	51.45	49.43	1.6
	228	302	39.64	318.62	321.79	318.26	1.7
	420	461	13.67	281.09	282.40	281.66	1.7
	633	750	8.37	115.92	118.67	115.47	2
1b	60	162	11.11	46.23	48.26	47.96	1.6
	237	308	32.10	255.81	262.28	259.38	1.8
	366	457	15.52	163.09	165.80	163.18	1.7
	641	780	12.36	131.03	133.12	130.92	1.7
2a	63	163	15.94	41.30	42.87	40.93	1.5
	214	298	41.62	403.88	404.51	403.20	1.7
	406	457	13.42	287.74	284.31	288.84	1.8
	611	707	11.38	112.14	110.57	111.79	1.8
2b	70	171	15.03	41.39	41.97	41.56	1.5
	222	306	41.48	327.52	324.60	324.90	1.8
	409	464	12.83	283.95	280.73	283.56	2
	631	708	10.74	114.97	117.77	114.55	1.7
3a	63	134	14.57	43.18	44.56	42.98	1.7
	220	419	70.97	56.54	60.41	56.52	1.6
3b	66	126	14.57	42.56	43.98	42.13	1.6
	222	440	62.30	53.53	54.13	53.23	1.6
4a	68	161	9.72	41.62	42.18	41.53	1.5
	229	371	53.71	340.24	339.47	341.18	1.6
	468	510	24.90	72.77	75.02	72.39	1.8
4b	66	163	12.96	43.09	44.26	43.56	1.6
	236	375	51.99	308.79	305.82	307.47	1.6
	472	530	17.68	71.34	74.98	72.32	1.8

*) T_i — initial degradation temperature, T_f — final degradation temperature, E_a — activation energy calculated with C-R (Coats—Redfern), F-W (Flynn—Wall method) or U-S (Urbanovici—Segal) method, n — reaction order.

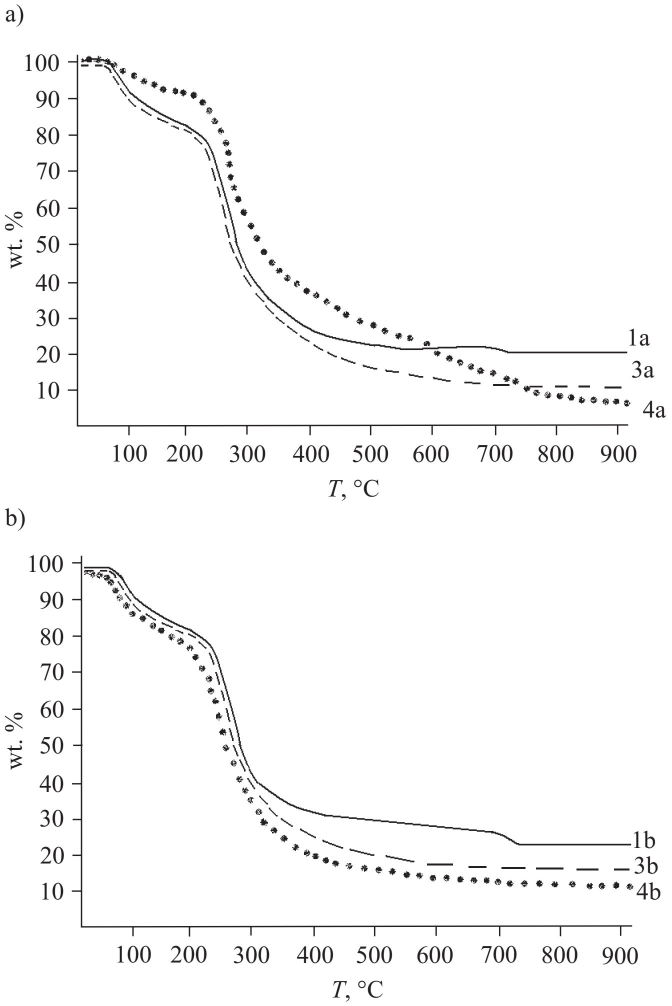


Fig. 4. TGA thermograms of microparticles based on the following complexes: a) 1a — Gll-Fe(III), 3a — Gll-Cu(II), 4a — Gll-Co(II), b) 1b — Gll + PVAL-Fe(III), 3b — Gll + PVAL-Cu(II), 4b — Gll + PVAL-Co(II)

microparticles in bidistilled water at 25 °C until the equilibrium was reached. The results plotted as swelling degree at equilibrium (S_{eq}, %) for the polymer-metal complexes are given in Figure 5.

So it can be seen, that the water swelling behavior of the microparticles based on the polymer-metal complex depends on two factors, namely the type of the metal used and the presence of PVAL. In the presence of metal ions the ionic crosslinked networks are formed, which could reduce the ability of the gellan molecules to interact with water and therefore, the swelling capacity is decreased. From Figure 5 and Table 1 it is also observed a good conformity between the sizes of microparticles based on polymer-metal complexes and their swelling capacities. For the microparticles based on Gll-PVAL the swelling degree decreased more probably due to the hydrogen bond between -OH groups belonging to PVAL and gellan, as well as the coordination of the metal ions with free electron pairs of the oxygen from the -OH groups belonging to PVAL. This behavior is a consequence of the less hydrophilic structure of these microparticles which is also found in the gels crosslinked by physical interactions.

Based on the Peppas equation (2) the kinetic parameters of swelling process of microparticles based on polymer-metal complexes were calculated and their values are given in Table 4.

The values of diffusion coefficient (n_d) were obtained by linear regression analysis. For spherical shape the value of $n_d = 0.43$ indicates Case I diffusion (Fickian), $0.43 < n_d < 0.85$ indicates anomalous diffusion (non-Fickian), $n_d = 0.85$ indicates Case II transport and $n_d > 0.85$ indicates Super Case II transport [19]. In the case of microparticles based on polymer-metal complexes, the values of the exponent n_d between 0.476 and 0.697 indicate a non-Fickian diffusion. Therefore, the swelling process of the microparticles based on polymer-metal complexes takes place

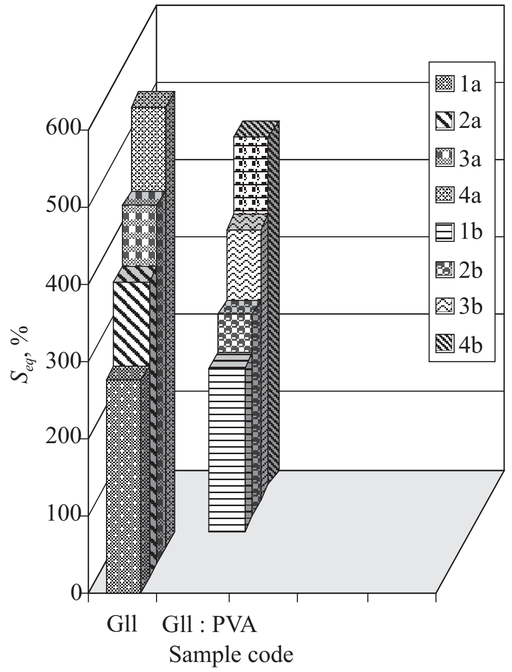


Fig. 5. Swelling behavior in water (S_{eq}, 25 °C) for the microparticles based on polymer-metal complexes (sample codes — see Table 1)

as a consequence of a combination of diffusion process and molecular relaxation.

Table 4. Kinetic parameters of the swelling process in water (at 25 °C)*)

Sample code (see Table 1)	S_{eq}, %	n_d	k	R^2
1a	276	0.578	0.2414	0.997
1b	210	0.558	0.3138	0.990
2a	384	0.492	0.2458	0.992
2b	260	0.476	0.2549	0.998
3a	461	0.542	0.2360	0.996
3b	350	0.498	0.1604	0.999
4a	570	0.697	0.1050	0.992
4b	451	0.542	0.1263	0.991

*) S_{eq} — swelling degree at equilibrium, n_d — diffusion coefficient.

CONCLUSIONS

The different types of microparticles based on the gellan or gellan:poly(vinyl alcohol) mixture and various metal ions were synthesized by ionotropic gelation which is a simple, convenient, fast and cheap method and also occurs in mild conditions. The complexes formation between Gll and Gll + PVAL mixture and metal ions was investigated with several methods. FT-IR spectra confirmed the interaction of Gll or Gll + PVAL mixture with metal ions. The incorporation of the metal ions (Fe^{3+}, Fe^{2+}, Co^{2+} and Cu^{2+}) into the polymer matrix led to the increase of thermal stability of these microparticles based on the polymer-metal complexes. The swelling degrees of microparticles in water depend on the metal ion and were found to be in the following order: $Fe^{3+} < Fe^{2+} < Cu^{2+} < Co^{2+}$.

Further experiments will be done to prove potential applications of these new materials in medicine or pharmacy.

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