



## Starch–metal complexes and their rheology

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**Abstract:** Changes in conductivity of 5 w/w% starch gels was studied on their titration with 0.1 M aqueous solutions of selected metal salts. Starch gels usually trapped around 10 mg metal ions per 1 g starch [Co(II), Cu(II), Fe(III), Ni(II)] and that value was only slightly dependent on starch origin (amaranthus, corn, potato, tapioca, waxy corn). Among salts studied (acetates, chlorides, nitrates) FeCl<sub>3</sub> and NiCl<sub>2</sub> were likely to be used because they hydrolyzed increasing conductivity of the solutions and formed micelles of corresponding hydroxides adhering to starch micelles and increasing amount of trapped metal. Addition of metal salts to starch gels had a devastating effect on pseudoplasticity and viscosity of starch gels and only potato starch gel was to a certain extent, exceptional in that respect.

**Key words:** amaranthus starch, corn starch, potato starch, tapioca starch, waxy corn starch.

### Introduction

There is fairly abundant number of reports describing Werner-type complexes of central metal ions with mono- and di-saccharides as O-ligands [1-11]. Consequently, also polysaccharides are capable as O-ligate metal ions [12-27]. Particular attention has been paid to starch as the ligand of metal ions. Relevant studies involved granular as well as pregelatinized starch of various botanical origin and numerous metal salts.

The phenomenon of coordination of metal ions to starch can influence metal ion uptake to living organisms and their excretion within the food chain and, therefore can affect life processes [28]. Coordination of metal ions to starch could be regarded as a positive phenomenon if starches are used as, e.g. aids for soil cementation [29-40], depressants in the flotation of complex metal ores [41,42], as well as binders and plasticizers in metal oxide based ceramics [43-45].

Problem of the coordination of starch to metal ions appeared to be more complex as counter ions of salts applied also strongly interact with starch [28, 46]. In case of granular starch additional factor has to be taken into account. On swelling, depending on the nature of the metal ion either cations or anions penetrate the granule interior. Thus, anions penetrate granular starch suspended in aqueous solutions of salts of metals of the first non-transition group [25]. In contrast to that, cations of the metals from higher non-transition [26] and transition groups [20] bound in granules by coordination as proven by EPR and thermal studies [13-20]. Starch gels more efficiently coordinate to metal ions and amylopectin more efficiently coordinate to

metal ions than amylose [17]. Potato starch (PS) and amylopectin additionally coordinate metal ions to the phosphate groups [19, 48].

In aqueous solutions, carbohydrate complexes with metal ions are fairly unstable because of low donor properties of the hydroxyl groups. Computations of gas phase basicity performed for the hydroxyl groups  $\alpha$ -D-glucose [49] point to the hydroxyl group at C6 as the most basic center of that saccharide. Ability to form complexes increases by several orders in acidic media [50]. There is a little selectivity between potential coordination sites in saccharides [11]. In polysaccharides the hydroxyl groups at C2 and C3 are also involved in coordination and that process does not influence the saccharide units conformation [27]. Disordered conformations of polysaccharide chains has a priority at low salt concentration but as concentration increases ordering of the macrostructure in complexes proceeds [51- 53].

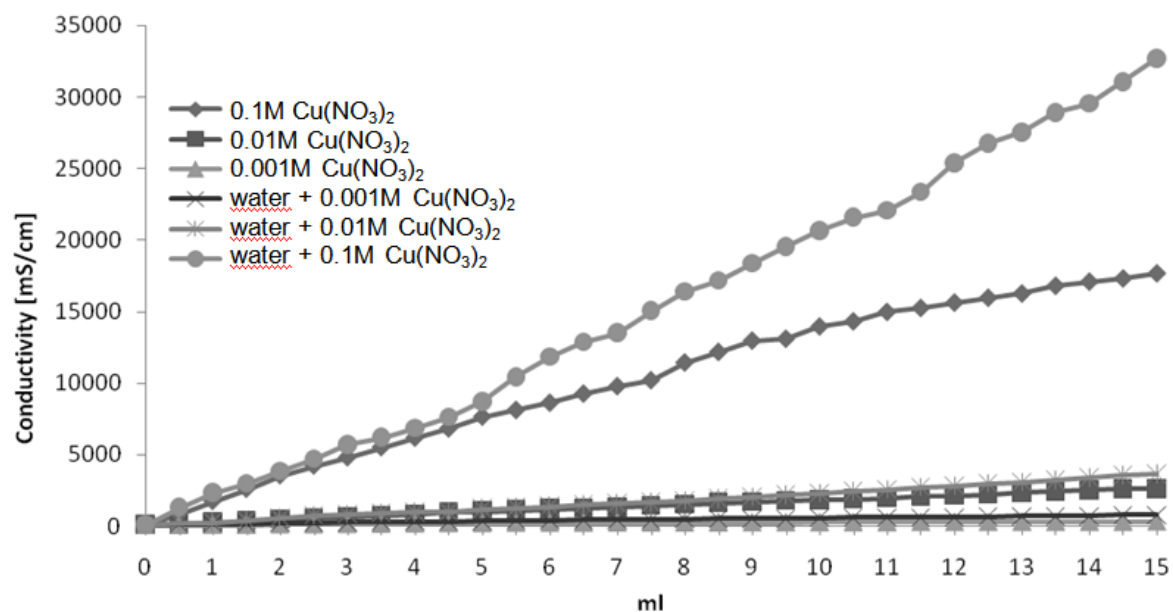
Our former EPR studies [16-20] showed that complexes of starches with all metal acetates, iron(III) chloride and all Ni(II) salts had tetrahedral inner coordination spheres. Cu(II) nitrate and chloride formed complexes of the square planar inner coordination spheres whereas Co(II) salts, except acetate had octahedral inner coordination spheres.

Although formation of the Werner-type complexes of metal salts with starches [16-20] has been proven and structures of inner coordination spheres of those complexes, enthalpies of their formation, and thermal stabilities have been reported, neither macrostructure of such complexes nor capacity of starches in coordinating metal ions was recognized. In this paper the problem is approached quantitatively involving conductivity and rheological measurements of starch pastes on addition of metal salts. The results contribute to the problem of possible use of starches in drilling mud, soil conditioning and other applications.

## Results and discussion

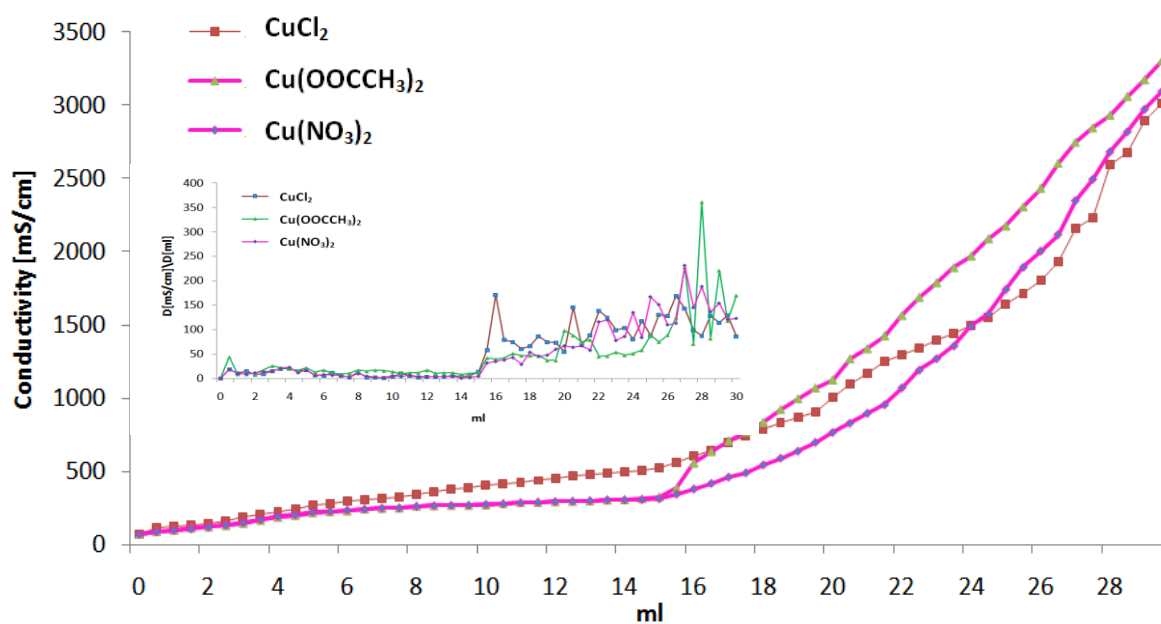
Starches – linear (amylose) and branched (amylopectin) polymers of  $\alpha$ -D-glucose, are polydentate ligands for metal ions. Because of their flexible macrostructure, only limited number of potential coordination sites of starch polysaccharides could be engaged in coordination to the central metal atom. Knowledge of the structure of metal complexes of monomeric  $\alpha$ -D-glucose [2-4] cannot be directly applied for considerations of the complexes of those metals with starch polysaccharides. It could not be even suggested whether ligation of the central metal atoms occurred in either intra- or intermolecular manner. Likely, both modes of coordination could take place. In case of PS, the problem was additionally complicated by involvement of the phosphato moiety from phosphoric acid esterifying every 8-12  $\alpha$ -D-glucose unit of amylopectin in its 6-CH<sub>2</sub>OH group. Such groups could also perform as O-ligand of the central metal atoms.

One could see from Fig. 1 that conductivity of solutions of PS with of Cu(NO<sub>3</sub>)<sub>2</sub> was always lower than that of solutions of plain salt of the same concentration. The effect observed could result either from a trapping ions by starch or from limited mobility of charge carriers in an environment of higher viscosity. A residual conductivity could be caused by ions occupying an outer coordination sphere of complexes.



**Fig. 1.** Influence of the concentration of a solution of the added salt on the conductivity of arrangements with potato starch (PS) 5% (w/w).

The course of the line for titration of PS paste with 0.01M solution of the copper salt clearly proceeded in three stages as seen in Fig. 2.



**Fig. 2.** Increase in conductivity of the 5 w/w% aq. solution of potato starch on its titration with 0.01 M solutions of copper(II) chloride, acetate and nitrate (and its first derivative).

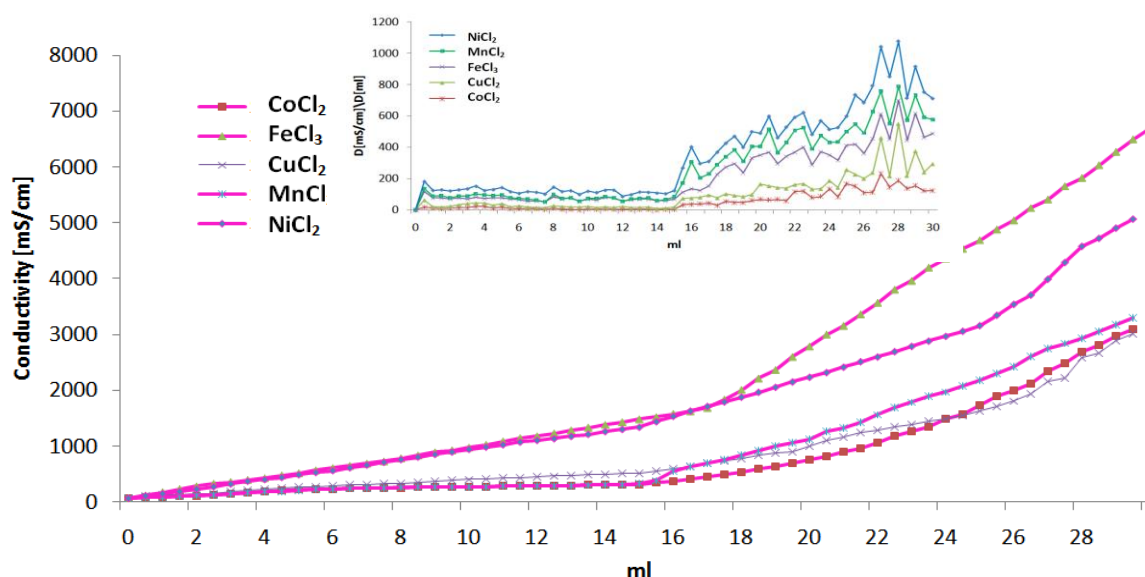
Initial stage involved apparently monotonous increase in conductivity of the paste. It was over when the dose of added salt exceeded about 4.5 mL. This stage was followed by a plateau in case of copper nitrate and acetate and a semi-plateau in

case of copper(II) chloride. Except the case of copper(II) nitrate in waxy corn starch (WCS), after consumption of approximately 15.5 mL of any of three copper salt there was a fast increase in conductivity of the solution. In the exceptional case of  $\text{Cu}(\text{NO}_3)_2$  in WCS the increase in the conductivity required 17 mL of the 0.01 M solution of that salt. That dose corresponded to an increase in amount of trapped metal ion from “regular” about 10 mg when 15.5 mL of salt solution was consumed to 11 mg per 1 g starch.

In case of titration of tapioca (TS), corn (CS) and amaranthus (AS) starches a monotonous increase in the conductivity up to the point of saturation was practically identical for all three copper(II) salts.

In spite of the highest viscosity of PS [54], the points of the saturation of other starches were situated at closely the same volume and conductivity value as in the case of PS. Thus, viscosity of solutions was not critical for the conductivity of solutions of complexes.

In PS and WCS gels the course of changes of conductance on titration with  $\text{CuCl}_2$  slightly differed from these recorded for titration with  $\text{Cu}(\text{NO}_3)_2$  and  $\text{Cu}(\text{OOCCH}_3)_2$ . First of all,  $\text{CuCl}_2$  provided higher conductivity. It almost monotonously increased up to the point of saturation after which each dose of titrating solution caused sharp increase in the conductivity. Such exceptional behaviour appeared common for Fe(III) and Ni(II) chlorides, although in WCS gel  $\text{NiCl}_2$  showed identical effect upon conductivity of solution as “well-behaving”  $\text{CoCl}_2$  and  $\text{CuCl}_2$ . Fig. 3 presents example of such behaviour for PS. Reasons of exceptional behaviour remain unclear and might be associated not only with ionic properties of solutions and structure of inner coordination spheres around the central atoms but also with specific structural properties of gelatinized starches, that is, ability to include ions in form of clathrates.



**Fig. 3.** Course of titration of potato starch with Co(II), Cu(II), Fe(III), Mn(II) and Ni(II) chlorides (and its first derivative).

Thus, in PS gel the point of saturation for titration with  $\text{NiCl}_2$  was located at 25.5 mL whereas for titration with  $\text{FeCl}_3$  that point corresponded to 17.5 mL. In both cases starch gel trapped more cations and anions and that could result not only from

coordination but also accompanied surface sorption and inclusion. On titration of CS gel with  $\text{NiCl}_2$  the saturation point was afforded at 15.5 mL of added solution whereas the saturation point for  $\text{FeCl}_3$  reached after addition of 17 mL of the solution. Corresponding points in WCS gel were located at 16.5 and 25 mL for  $\text{FeCl}_3$  and  $\text{NiCl}_2$ , respectively. In TS gels these points appeared at 18 and 15.5 mL, respectively, and in AS gel titration also proceeded abnormally. The line of titration with  $\text{FeCl}_3$  exhibited two saturation points, that is, those corresponding to 11.5 and 25.5 mL of added solution and the sole saturation point on the line of titration with  $\text{NiCl}_2$  corresponded to 17 mL of added solution.

With certain exception for nickel(II) acetate in WCS gel, other nickel salts than chloride contributed to conductivity of starch gels in identical manner as did other salts and quantitatively all starch gels trapped the same amount of those salts in the point of saturation.

In summary of this part of study one could state that in majority of cases the titration of starch gels with solutions of  $\text{FeCl}_3$  and  $\text{NiCl}_2$  proceeded differently than in other cases. Table 1 summarizes results of titration of starches with 0.01 M aqueous solutions of selected metal salts.

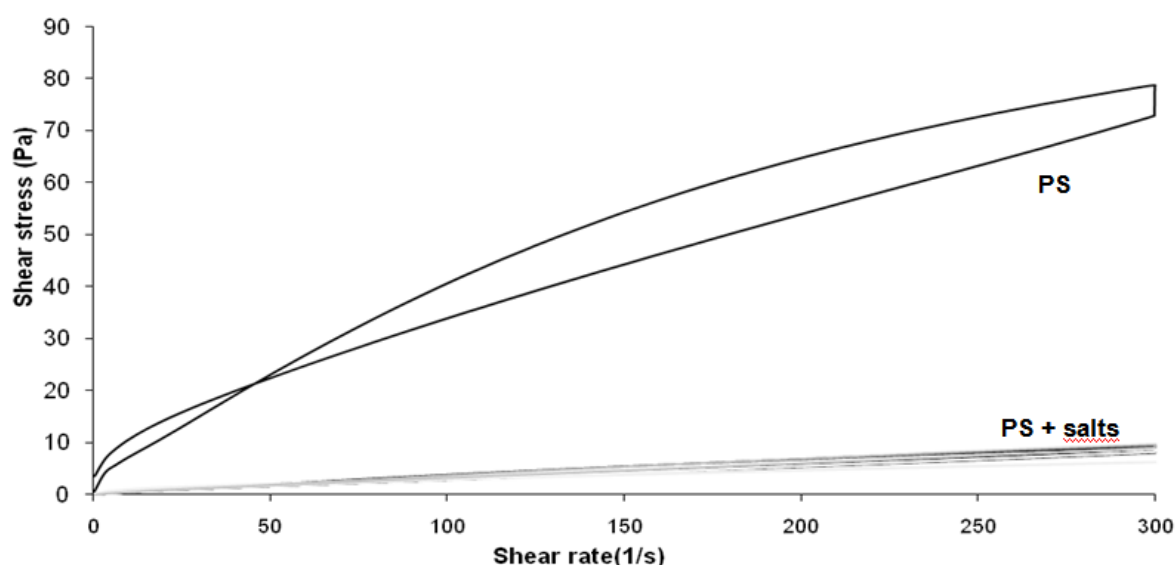
**Tab. 1.** Results of titration of 5 %w/w gels of starches with 0.01 M aqueous solutions of selected metal salts.

| Saturation volume [mL] | Salt                                 | mg cation/g starch | Starch variety      |
|------------------------|--------------------------------------|--------------------|---------------------|
| 11.5                   | $\text{FeCl}_3$                      | 6.4                | AS                  |
| 15.5                   | $\text{Co}(\text{NO}_3)_2$           | 9.1                | AS, CS, PS, TS, WCS |
|                        | $\text{Co}(\text{CH}_3\text{COO})_2$ | 9.1                | AS, CS, PS, TS, WCS |
|                        | $\text{CoCl}_2$                      | 9.1                | AS, CS, PS, TS, WCS |
|                        | $\text{Cu}(\text{NO}_3)_2$           | 10                 | AS, CS, PS, TS      |
|                        | $\text{Cu}(\text{CH}_3\text{COO})_2$ | 10                 | AS, CS, PS, TS, WCS |
|                        | $\text{CuCl}_2$                      | 9.5                | AS, CS, PS, TS, WCS |
|                        | $\text{FeCl}_3$                      | 8.7                | PS, WCS             |
|                        | $\text{Ni}(\text{NO}_3)_2$           | 9.1                | AS, CS, PS, TS, WCS |
|                        | $\text{Ni}(\text{CH}_3\text{COO})_2$ | 9.1                | AS, CS, PS, TS, WCS |
|                        | $\text{NiCl}_2$                      | 9.1                | CS, TS              |
| 17                     | $\text{Cu}(\text{NO}_3)_2$           | 10.8               | WCS                 |
|                        | $\text{NiCl}_2$                      | 10                 | AS                  |
| 17.5                   | $\text{FeCl}_3$                      | 9.8                | CS                  |
| 25.5                   | $\text{FeCl}_3$                      | 14.2               | AS                  |
|                        | $\text{NiCl}_2$                      | 15                 | WCS                 |
| 27.5                   | $\text{FeCl}_3$                      | 15.35              | TS                  |

Higher conductivity of the solutions could result from hydrolysis of those chlorides. Because all starch gels indicated  $\text{pH} > 7$  these chlorides could turn into hydroxides which prior to dehydration, in micelle form could adhere to micelles of starch. It could explain the shift of the saturation point to higher values. Because such behavior was not common for all starch gels specific properties of starch gels in respect to binding metal salts had to be taken into account. Certainly, anionic character of PS had no essential effect on binding metal salts. Also, as mentioned above, viscosity of starch gels did not affect the course of titration. It is known [55] that CS gel always contains residual lipids but, generally, they also do not affect the course of titration. Thus, macrostructure of starch in gels and, for instance, their specific tendency to retrogradation [56], dependent also on metal ions, could be one of the factors producing exceptions observed on titration of starch gels with metal salt solutions.

### *Rheological studies of complexes of starch with salts of metals*

Admixture of any metal salt solution dramatically reduced pseudoplasticity of PS gels and their thixotropy and the nature of the salt in the solution of the same concentration had only a subtle effect on the observed phenomenon (Figs 4 and 5).



**Fig. 4.** Dependence of shear rate on shear stress for potato starch and its complexes with metal salts (0.1 M solutions).

Similarly, the effect of the nature of the cation of added salt had a negligible effect upon pseudoplasticity and thixotropy of resulting systems. All of them almost equally and efficiently affected these properties.

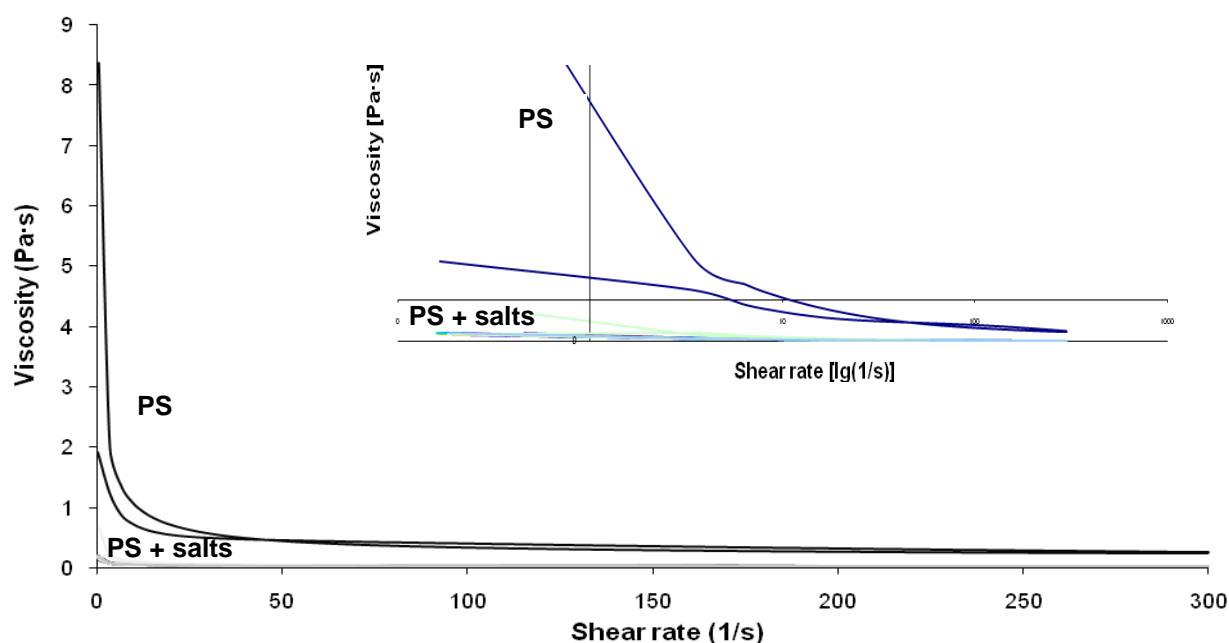
Such results indicated that the coordination to the metal ions really ruined the formerly postulated network of the starch gels.

Comparative studies to confirm these results were carried out only for PS gels with  $\text{Cu}(\text{NO}_3)_2$  of concentrations varying from 0.5 to 0.0001 M. Fig. 6 demonstrates the shear rate on shear stress dependence for these cases. Reduction of the pseudoplasticity increased with salt concentration in the system. Dramatic decrease in the shear stress after admixture of salts could suggest that the coordination sphere around the central metal atom was occupied by the D-glucose units of the same

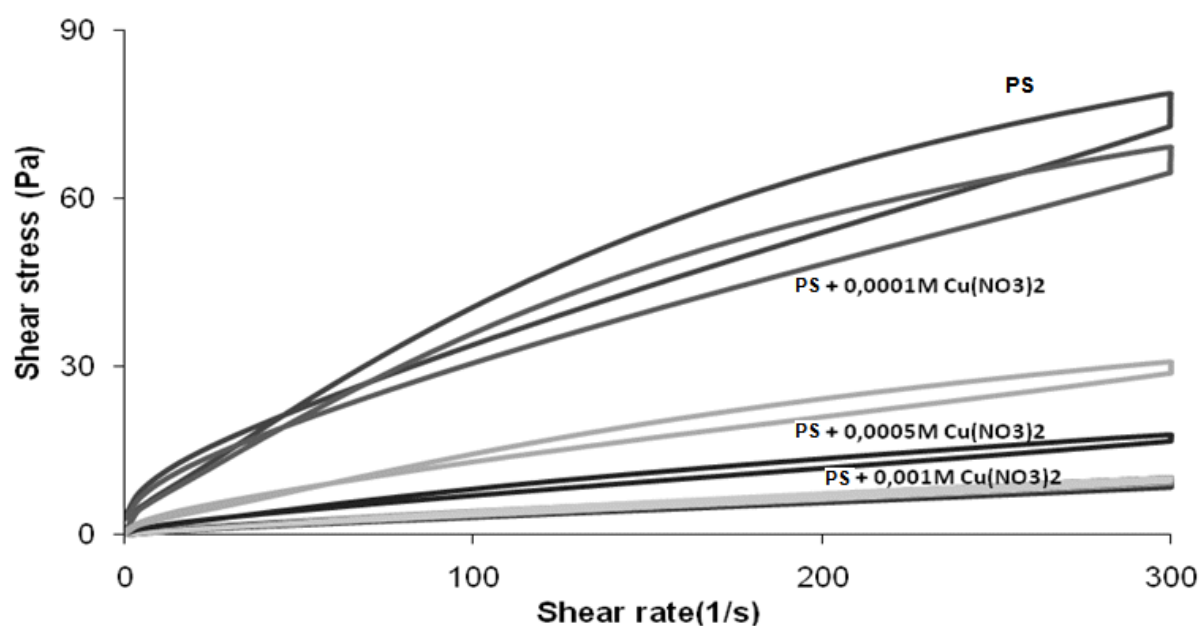


molecule of polysaccharide leading to the formation of globular structures. The latter would be unable to form a stable, rigid network of the gels.

The effect of the coordination on the rheological properties of the systems containing various central metal atoms depended not only on the salt concentration (Table 2) but also on the counterions (Table 3) as demonstrated in form of results of fitting rheological data to the Herschel-Bulkley model. In terms of  $R^2$  the fitting is perfect.



**Fig. 5.** Dependence of shear rate on viscosity for potato starch and its complexes with metal salts (0.1 M solutions).



**Fig. 6.** Dependence of shear rate on shear stress for potato starch and its complexes with metal salts (0.1-0.5 M and 0.01-0.0001 M).

**Tab. 2.** Rheological properties of complexes of potato starch with Cu(II) nitrate (15 ml of 0.0001-0.5 M nitrate). (Means of two estimations)<sup>a</sup>

| Cu(NO <sub>3</sub> ) <sub>2</sub><br>[M] | Herschel-Bulkley parameters |       |               | $\eta_{100}$ [Pa·s] | Hysteresis area<br>[W·m <sup>-3</sup> ] |
|--|-----------------------------|-------|---------------|---------------------|---|
|  | K [Pa·s <sup>n</sup> ]      | n [-] | $\tau_0$ [Pa] |                     |   |
| None                                     | 1.93±0                      | 0.66  | 0.01          | 0.4                 | 1980.50                                 |
| 0.0001                                   | 1.78                        | 0.65  | 0.05          | 0.36                | 1561.00                                 |
| 0.0005                                   | 0.51                        | 0.73  | 0.01          | 0.14                | 551.45                                  |
| 0.001                                    | 0.27                        | 0.74  | 0.05          | 0.08                | 354.15                                  |
| 0.01                                     | 0.09                        | 0.83  | 0.01          | 0.04                | 177.00                                  |
| 0.1                                      | 0.07                        | 0.85  | 0.05          | 0.04                | 154.00                                  |
| 0.2                                      | 0.09                        | 0.82  | 0.04          | 0.04                | 146.70                                  |
| 0.3                                      | 0.14                        | 0.77  | 0.12          | 0.04                | 47.99                                   |
| 0.4                                      | 0.05                        | 0.92  | 0.23          | 0.04                | 32.57                                   |
| 0.5                                      | 0.06                        | 0.88  | 0.17          | 0.04                | 57.76                                   |

<sup>a</sup>R<sup>2</sup> in every case is 1.00

**Tab. 3.** Rheological properties of complexes pasted potato starch with salts (15 mL of 0.1M solutions) of various metals of transition groups.

| Added salt                           | Herschel-Bulkley model |       |               | R <sup>2</sup> | $\eta_{100}$<br>[Pa·s] | Area of<br>hysteresis<br>[W·m <sup>-3</sup> ] |
|--------------------------------------|------------------------|-------|---------------|----------------|------------------------|---|
|                                      | K [Pa·s <sup>n</sup> ] | n [-] | $\tau_0$ [Pa] |                |                        |   |
| None                                 | 1.93±0.13              | 0.66  | 0.01          | 0.9966         | 0.41                   | 1980.5  |
| Co(NO <sub>3</sub> ) <sub>2</sub>    | 0.06                   | 0.86  | 0.01          | 0.9997         | 0.03                   | 147.4   |
| Co(OOCCH <sub>3</sub> ) <sub>2</sub> | 0.04                   | 0.94  | 0.09          | 0.9993         | 0.03                   | 137.5   |
| CoCl <sub>2</sub>                    | 0.05                   | 0.92  | 0.08          | 0.9995         | 0.03                   | 147.3   |
| Cu(NO <sub>3</sub> ) <sub>2</sub>    | 0.08                   | 0.84  | 0.00          | 0.9999         | 0.04                   | 154.0   |
| Cu(OOCCH <sub>3</sub> ) <sub>2</sub> | 0.06                   | 0.88  | 0.10          | 0.9997         | 0.03                   | 111.7   |
| CuCl <sub>2</sub>                    | 0.06                   | 0.87  | 0.02          | 0.9999         | 0.03                   | 111.7   |
| FeCl <sub>3</sub>                    | 0.13                   | 0.66  | 0.39          | 0.9994         | 0.03                   | 61.7  |
| Ni(NO <sub>3</sub> ) <sub>2</sub>    | 0.08                   | 0.83  | 0.05          | 0.9998         | 0.04                   | 138.0   |
| Ni(OOCCH <sub>3</sub> ) <sub>2</sub> | 0.07                   | 0.85  | 0.00          | 0.9997         | 0.04                   | 178.8   |
| NiCl <sub>2</sub>                    | 0.04                   | 0.96  | 0.13          | 0.9999         | 0.03                   | 112.9   |

The least critical reduction of the consistency coefficient, K in the Herschel-Bulkley equation (1)

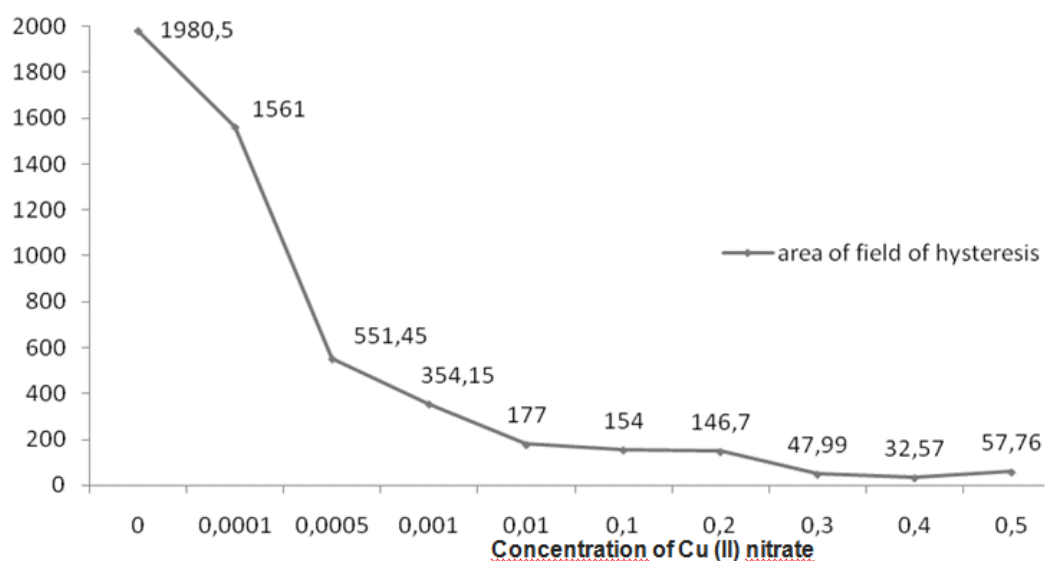
$$\sigma = K(\dot{\gamma})^n + \tau_0 \quad (1)$$

where n is the flow behaviour index and  $\tau_0$  is the yield stress was found in case of admixing the most readily hydrolysing salt, FeCl<sub>3</sub>. Thus, acid-catalyzed hydrolysis of starch in constituting rheological properties of the coordinated gels was of minor importance.

In the experiment, K coefficient remained positive, n index ranged between zero and unity, and yield stress was slightly above zero. Thus, according to the Herschel Bulkley classification [57], gels from starch with coordinated metal salts have been situated on the borderline between pseudoplastic (shear-thinning) and Herschel-Bulkley fluids.



There are 4 areas of changes of the surface area of the hysteresis depending on the concentration of Cu(II) nitrate, i.e. 0-0.0001, 0.0001-0.0005, 0.0005-0.01, 0.01-0.2 and 0.2-0.5 (Fig. 7). First three stages might correspond to subsequent deterioration of the gel network as more hydroxyl groups of the gel coordinate to the central metal atoms. Concentration of the Cu(II) ions in 0.01 M solution of the applied volume of solution satisfied all coordination centers and admixture of further amount of the salt solution only slightly affected the already built gel structure. The small increase in the hysteresis loop of the gel could result from the formation of interglobular links as a result of coordination of selected peripheral hydroxyl groups on the surface of globules.



**Fig. 7.** Dependence area of field of hysteresis on concentration of Cu(II) nitrate in potato starch complexes (15 ml of 0.1 M solution).

The hysteresis loop depended to a certain extent on starch variety. Only plain gel of PS and such gel containing admixture of 0.001 M aq. solution of Co(II) nitrate demonstrated a hysteresis loop. Rheological properties of gels of other starches and their blends with solutions of Co(II) nitrates had a very low shear stress and the shear stress – shear rate relationship were plain without any considerable hysteresis loop.

## Conclusions

In conclusion, amount of metal ions trapped by starch, usually between 9 and 10 mg/g starch, is generally independent of its botanical origin. Except selected metal chlorides ( $\text{FeCl}_3$  and  $\text{NiCl}_2$ ) amount of trapped metal ions is independent of salt counterion. Metal cations destroy the starch gel network and as for their rheological properties, resulting metal coordinated gels are on the borderline between pseudoplastic and Herschel-Bulkley fluids.

## Experimental

### Materials

**Starches:** Potato starch (PS) Superior, isolated in Namysłów Potato Enterprise in 1997 followed all parameters according to Polish Standards [58], cornstarch (CS),

waxy cornstarch (WCS), amaranthus starch (AS), tapioca starch (TS), were kindly provided by Centralne Laboratorium Przemysłu Ziemniaczanego in Luboń at Poznań.

*Transition metal salts:*  $\text{Co}(\text{NO}_3)_2$ ,  $\text{Cu}(\text{NO}_3)_2$ ,  $\text{Ni}(\text{NO}_3)_2$ ,  $\text{Co}(\text{CH}_3\text{COO})_2$ ,  $\text{Cu}(\text{CH}_3\text{COO})_2$ ,  $\text{Mn}(\text{CH}_3\text{COO})_2$ ,  $\text{Ni}(\text{CH}_3\text{COO})_2$ ,  $\text{CoCl}_2$ ,  $\text{CuCl}_2$ ,  $\text{FeCl}_3$ ,  $\text{MnCl}_2$ ,  $\text{NiCl}_2$ ,  $\text{CoSO}_4$ ,  $\text{Cr}_2(\text{SO}_4)_3$ ,  $\text{CuSO}_4$ ,  $\text{Fe}_2(\text{SO}_4)_3$ ,  $\text{MnSO}_4$ , all of analytical grade were purchased from POCh Gliwice (Poland).

Ethanol of analytical grade was also purchased from POCH, Gliwice (Poland)

## Methods

### -Starch gelatinization and conductivity measurement

Starch (1g) was suspended in distilled water (40 mL) and agitated at 450 rpm for 10 min. The dispersion was then heated at 96 °C for 20 min continuing agitation. After cooling to room temperature 0.01 M aqueous solution of a metal salt (15 mL) was added in 0.5 mL doses. After each subsequent dose the solution was agitated for 1 min then conductivity was measured with InoLab level 2 conductometer (Pol-Eko-Aparatura (Wodzisław Śląski, Poland). Residual conductivity was 0.325, 0.261, 0.287, 0.333 and 0.372 mS/cm for PS, CS, WCS, TS, and AS gels, respectively.

### -pH measurements

Measurements were performed at 25 °C for 5 w/w% aqueous solutions of starch gels and for 0.01M aqueous solutions of salts. The following values were recorded: 7.12, 8.34, 8.72, 8.27 and 8.19 for PS, CS, WCS, TS and AS gels, respectively. pH of salt solutions is given in Table 4.

**Tab. 4.** pH of 0.01 M aqueous solutions of salts.

|          | Co(II) | Cu(II) | Fe(III) | Ni(II) |
|----------|--------|--------|---------|--------|
| Chloride | 6.23   | 5.34   | 2.67    | 6.39   |
| Nitrate  | 7.93   | 6.13   |         | 6.45   |
| Acetate  | 8.07   | 6.39   |         | 6.78   |

### -Gelatinized starches with metal salts for rheological studies and rheology measurements

Aqueous 0.2 M salt solutions were prepared from  $\text{Co}(\text{NO}_3)_2$ ,  $\text{Cu}(\text{NO}_3)_2$ ,  $\text{Ni}(\text{NO}_3)_2$ ,  $\text{CoCl}_2$ ,  $\text{CuCl}_2$ ,  $\text{FeCl}_3$ ,  $\text{MnCl}_2$ ,  $\text{NiCl}_2$ ,  $\text{Co}(\text{CH}_3\text{COO})_2$ ,  $\text{Cu}(\text{CH}_3\text{COO})_2$ ,  $\text{Mn}(\text{CH}_3\text{COO})_2$ , and  $\text{Ni}(\text{CH}_3\text{COO})_2$ . Additionally, 0.0001, 0.0005, 0.001, 0.01, 0.1, 0.3, 0.4, and 0.5 M aqueous solutions were prepared from  $\text{Cu}(\text{NO}_3)_2$ . They were admixed (10 mL) to a gel prepared from a starch (1g) in distilled water (40 mL) as described in procedure given above. After blending gel with a salt solution, resulting blend was agitated in room temperature for 10 min prior to experiment.

Samples were placed into measuring system of a Rheostress RS1 (Gebrueder Haake, GmbH, Karlsruhe, Germany) rheometer where they were conditioned at 25 °C for 3 min. The measuring system Z34 comprised of two coaxial cylinders. Measurement was carried out at 25 °C in the CR (controlled shear rate) mode. Shear

rate was increased from 0 to 300 s<sup>-1</sup> in 5 min and maintained for 1 min followed by 5 min decrease to the point of origin. Measurements were run in duplicates. Rheo Win 2.97 software provided calculation of area of the hysteresis loop from the results of the measurements and fitting the measurement points to the Herschel-Bulkley model.

#### -Calculations of metal ions trapped by starches

Amount of metal ions trapped by particular starches was calculated based on the volume of 0.01 M aqueous solution of metal salt consumed to reach the saturation point after which a fast increase in the conductivity took place.

#### -Statistics

Statistica 7 (Statsoft, Inc., Tulsa, OK., USA), software was used. One-factorial analysis of variance (Duncan test) at  $p < 0.05$ .

#### Abbreviations

PS – potato starch  
TS – tapioca starch  
CS – corn starch  
AS – amaranthus starch  
WCS – waxy corn starch

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