

Production and Properties of Native Potato Starch-Coated Urea

Rasa PALECKIENĖ*

Department of Physical and Inorganic Chemistry, Faculty of Chemical Technology, Kaunas University of Technology, Radvilenu str. 19 – C'242, Kaunas LT - 50254, Lithuania

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This work is dedicated to researching the possibilities of using starch coating for slow-release fertilizers. Urea was used as nitrogen containing component, because it is the most suitable for the production of slow-release nitrogen fertilizers and has the highest concentration of nitrogen – 46.6 %. During the studies, native potato starch film was prepared and its stability was evaluated, subsequently, urea was coated with starch film/coating and the influence on properties of fertilizer granules (hygroscopicity and strength) was evaluated. Single and/or multiple layered films were formed during the coating process and the influence of coating thickness on urea solubility was researched. It was found that the mechanical properties of urea with double coating change quite insignificantly while coating reduces the solubility of urea by more than 20 %.

Keywords: starch, coating, urea, slow-release fertilizers, properties.

1. INTRODUCTION

Many traditional mineral fertilizers, especially the ones containing nitrogen, are well soluble in water so the plants can absorb nutrients in a short period. However, such fertilizers have some drawbacks: due to high solubility, some nutrient losses may occur so plants would receive only 30–50 % of nutrient input [1]. Ammonium salts, nitrates, urea, and other compounds dissolve quickly due to rain and are washed out of the soil by groundwater and surface water. This causes significant environmental problems because groundwater enters drainage ditches and pollutes rivers, lakes, etc. To avoid these drawbacks and completely or partially reduce the losses in the fertilizer industry, special fertilizers and their modifications are developed – slow-release/controlled-release fertilizers and fertilizers stabilized with nitrification and urease inhibitors [2–4].

According to statistics provided by International Fertilizer Organisation (IFA), the annual consumption of synthetic slow-release fertilizers (SRF) in the world comprises 562 000 tonnes, which represents about 0.15 % of the total world fertilizer consumption [4, 5]. SRF is considerably more expensive than traditional fertilizers and this severely limits their usage. Intensive scientific research and development of slow-release fertilizers were conducted in the US, Germany, Japan, and elsewhere [1, 3, 4] to reduce the cost of such fertilizers and expand their assortment.

The most common of all slow-release fertilizers are nitrogen fertilizers. The literature survey provides many effective methods to slow down the leaching of nitrogen from fertilizer granules. One of the most popular and most common ways to control the operation of the fertilizer is the production of coated/encapsulated fertilizers. In this case, nutrient release is controlled by a physical barrier. This method allows to reduce the solubility of fertilizers and increases absorption time of nutrient. The surface of

granules, which is not entirely smooth, is coated with a film of coating material whose amount (thickness) proportionally prolongs the duration of nutrient intake. The coating can be performed using various materials, but the most widely applicable and known coated fertilizers are obtained by coating with sulfur (Sulfur-Coated Urea, SCU), with polymers (Polymer Coated Fertilizers, PCP), or with layers of sulfur and polymer (Polimer-Sulphur Coated Fertilizers, PSCF) [4, 6–8]. The rate and the mechanism of nutrient release from coated granules process depend on the nature of the coating, its thickness as well as capillary diffusion of the solvent and the solution. The most efficient technique is coating of granules with synthetic polymers, but such films usually do not decompose in the soil and cause serious environmental pollution problems because macromolecular fragments of synthetic polymer remain in the soil.

Therefore, more attention is paid to biodegradable (BP) polymers recently [3, 9]. In agriculture, their application is constantly increasing. When BP enters the soil, their degradation starts because of the presence of bacteria, fungi, and algae enzymes also due to the process of chemical hydrolysis [10]. Among all the biopolymers starch is the most interesting. Starch is naturally synthesized by plants, it is completely biodegradable, is able to polymerize after some processing, is relatively inexpensive and its abundance is sustainable [9]. Starch is composed of two polysaccharides – amylose and amylopectin whose solubility in water is limited [11]. The properties of the starch film depend on the content of amylose and preparation conditions. The literature [3, 8–12] survey shows that starch is a material suitable for the production of fertilizers. The production process of the polymer coating is quite simple and films are rather resistant to moisture and mechanical loads. It is also possible to choose the different compositions of the starch to obtain the desired properties

* Corresponding author. Tel.: +370-37-457070; fax: +370-37- 300152.
E-mail address: rasa.paleckiene@ktu.lt (R.Paleckienė)

of the polymeric film. To obtain a more elastic film, plastification can be applied. There are some studies researching the solubility decrease of urea when added into the matrix of the starch-based polymer [11, 12] or using a combined coating of urea with starch and polyacrylic acid [13, 14]. The production of slow-release fertilizers with a biodegradable coating is a big step towards organic farming. Thus, to produce slow-release fertilizer which both contains a large amount of nitrogen and is environmentally friendly, urea should be used as a source of nitrogen (46.6 % nitrogen) and the surface of those granules should be coated with starch film as a biodegradable polymeric material.

The aim of this work is to explore the possibilities of application of native potato starch coating in the production of slow-release fertilizers.

2. EXPERIMENTAL DETAILS

Reagent and technical (SC "Achema", Lithuania) grade urea were used in the study – $\text{CO}(\text{NH}_2)_2$. Starch films were prepared by mixing 2.5 g of potato starch (Beroxfood, Germany), 2 ml of 50 % aqueous solution of glycerol ($\text{C}_3\text{H}_8\text{O}_3$ Glycerol anhydrous p.a. Reachem Slovakia), 3 ml of 0.1 M hydrochloric acid, and 25 ml of distilled water in 100 ml Erlenmeyer flask and heating it for 15 minutes at temperature 105–110 °C until a homogeneous solution is formed. The hot and viscous reaction solution is neutralized by adding 3 ml of 0.1 M sodium hydroxide solution. After cooling (down to 50–60 °C) the reaction mixture is immediately used to prepare films and to coat the urea granules. The drying time of the film depends on the temperature and the thickness of the film.

Experimental studies of urea solubility conducted to evaluate the effect of the coating of the starch film were carried out according to slightly modified guidelines presented in the research article [15] and recommendations [16]. Solubility was examined by mixing 1 g of the product with 10 g of quartz sand. The mixture is then placed into sintered glass filter (IIOP 169) with a pore diameter of 100–160 μm . Dissolution testing is performed with 50 ml of distilled water which is slowly (2 ml/min) administered through the layer of examined material. The remaining water is drawn off by a vacuum pump. Nitrogen content in the collected filtrate is determined by standard techniques [17, 18]. Amidic form nitrogen was determined by spectrophotometric measurements [19] carried out with T70+UV/VIS spectrometer (PG Instruments Ltd.). Interaction between urea and dimethylaminobenzaldehyde resulted in forming a coloured complex which absorbance was measured at 420 nm wavelength using a 1 cm cuvette (accuracy ± 0.004 Abs). Depending on the repeatability, investigation of the composition or properties of the same sample was performed 3–5 times and the arithmetic mean of the determined values is presented in this study.

Properties (hygroscopic moisture, pH) of coated fertilizer were determined by using the standard procedures [18]. The granulometric composition as granule size distribution was determined by sieve analysis of a sample and standard "Retsch" sieves (DIN-ISO 3310/1) were used. The static crushing strength of granules, as the medium value of granules crushing, was determined by using a device IPG-2. Its measurement range was 5–200 N, margin

error ± 2.00 % from the upper limit of measurement (when the temperature is 20 ± 5 °C). Calculations were made using a standard methodology [18, 20]. SEM analysis was carried out using scanning electron microscope PhenomWorld ProX (G5) to determine particle form.

Coated granulated product X-ray radiation diffractive analysis [21] was carried out by X-ray diffractometer DRON-6 (Cu K_α radiation, Ni filter, detector's step length – 0.02°, duration of intensity measurement in the step – 0.5 s, voltage $U = 30$ kV, current $I = 20$ mA).

Simultaneous thermogravimetric and differential scanning calorimetry (STA) [21–23] was carried out by the thermal analyser "LINSEIS STA PT-1000" (Germany). DSC-TGA parameters: temperature increase rate – 10 °C/min, range – 25–300 °C, crucibles – extruded aluminum, standard – the empty crucible, the atmosphere in the furnace – nitrogen N_2 20 mL/min, sample weight 1.6 mg. Measurement accuracy ± 3 °C.

IR spectra [22, 24] were obtained on a Perkin Elmer FT-IR spectrometer. The samples were produced by pressing the tablets from the test substance and the optically pure dried KBr. The tablet was prepared by mixing 1 mg of the test substance and 200 mg of potassium bromide.

3. RESULTS AND DISCUSSION

First of all starch film stability assessment was performed. Stability was evaluated by examining film solubility in different solutions. Films were cut and pieces of 1 cm^2 area samples were prepared to weigh ± 0.1 mg. Samples then were soaked in distilled water, acidified water (nitric acid, pH = 5), and 10 % urea (pH = 8.45) solution at 20 ± 2 °C. After 7 days the samples were removed from the solution, dried for 1 day at room temperature (~ 25 °C), then dried in the heating oven at 105 °C until constant weight is reached. The smallest change in mass ~ 10 % is observed when the starch sample was soaked in distilled water. Placing samples into the acidic aqueous solution (at pH = 5) resulted in film losing more weight ~ 14 %. The biggest weight loss occurred in 10 % urea solution: 18.8 % after 7 days.

Since it is known, that macromolecular compounds swell before dissolving, more detailed evaluations of starch film stability were needed. In this case influence of fertilizer components (NH_4NO_3 , KH_2PO_4 , $\text{CO}(\text{NH}_2)_2$) and the pH of the medium on the stability was investigated. Solutions of different salt concentrations were prepared 1, 5, 10 and 15 %, and the pH of these solutions were measured. Solutions were used to determine the degree of swelling of starch film samples which were cut into 1.5×1.5 cm pieces. The degree of swelling of starch film samples after 15 minutes were calculated:

$$\alpha = \frac{m_2 - m_1}{m_1}, \quad (1)$$

here m_1 is the mass of dry film, g; m_2 is the mass of swollen film, g. Results are presented in Table 1. The obtained results show, that when placed into ammonium nitrate and urea solutions, the degree of swelling of the starch film increases with increasing pH and hence the salt concentration. Potassium dihydrogen phosphate solution has a similar effect – though increased salt concentration

results in lower pH value, the degree of swelling in these solutions decreases (~1).

Table 1. Degrees of swelling of starch in different solutions

| Concentration of solution, % | 1 | 5 | 10 | 15 |
|---------------------------------------|------|------|------|------|
| NH₄NO₃ | | | | |
| pH of solution | 5.2 | 5.25 | 5.40 | 5.45 |
| α | 1.00 | 1.34 | 1.97 | 2.68 |
| KH₂PO₄ | | | | |
| pH of solution | 4.5 | 4.3 | 4.2 | 4.15 |
| α | 1.00 | 1.09 | 1.07 | 1.06 |
| CO(NH₂)₂ | | | | |
| pH of solution | 6.95 | 7.95 | 8.45 | 8.75 |
| α | 1.03 | 1.52 | 1.81 | 2.32 |

Performed dissolution-swelling studies suggest that the stability of starch films is sufficient enough at different pH and concentrations of salt solutions thus they can be used in further research – coating granules.

Technical grade urea was used for coating with starch polymeric substance (PS) produced from potato starch. The only a fraction of urea granules of 2–3 mm in size was used for coating. After the coating process granules were dried in the heating oven at 65 °C for 5 hours. Granules then were removed, weighed and similar size, as well as evenly coated granules were selected for further experiments. To assess the influence of coating thickness and to achieve a better overall covering, coating conditions were slightly modified – the addition of dry starch (St) was applied as filler into starch polymeric substance. General sample preparation process: 10 g of technical grade urea granules (or single-layered granules) were mixed with 1 g of starch polymer substance or 1 g of starch polymer substance with the addition of 0.5 g of dry starch. Sample preparation conditions and the measured content of nitrogen are presented in Table 2.

Table 2. Conditions of sample preparation and content of amidic form nitrogen

| No. | Name of sample | Composition, g | | | Content of amidic form nitrogen, % | | | |
|-----|----------------|----------------|----|-----|------------------------------------|------|------|---------|
| | | Urea | PS | St | 1 | 2 | 3 | Average |
| 1 | Urea | 10 | – | – | 46.2 | 46.0 | 46.1 | 46.1 |
| 2 | Urea+PS | 10 | 1 | – | 43.1 | 42.8 | 41.2 | 42.4 |
| 3 | Urea+2PS | 10 | 2 | – | 38.2 | 38.6 | 38.7 | 38.5 |
| 4 | Urea+(PS+St) | 10 | 1 | 0.5 | 40.9 | 40.3 | 40.3 | 40.5 |
| 5 | Urea+2(PS+St) | 10 | 2 | 1 | 35.5 | 35.3 | 35.1 | 35.3 |

With the increase the amount of coating materials used for urea covering, the content of nitrogen in the samples decreases. All coated samples were tested for static strength and received results were compared with the strength of technical grade urea granules as shown in Fig. 1.

The obtained results show that static strength of the granules depends on coating thickness as well as composition. The application of a single layer of starch substance increased the static strength of granules up to 22.7 N/gran, while two-layered granules have somewhat reduced strength (20.5 N/gran which is still higher than the strength of technical grade urea (20.35 N/gran). When granules are covered with a combined film consisting of

starch substance and dry starch as filler, their strength decreases down to 19.9 and 19.3 N/gran.

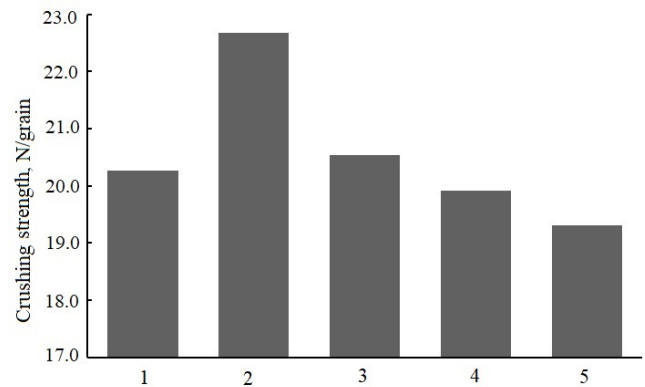


Fig. 1. The static crushing strength of technical grade urea (No. 1) and coated samples (No. 2–5)

While the strength of the aforementioned granules is the lowest, but their values are still higher than the minimum requirements provided by fertilizer producers – 7.0 N/gran [25]. It is very important to avoid the breakage of granules during all stages: production, storage, and transport.

The study was continued with moisture sorption experiments. These experiments were carried out at 20 °C by placing the samples in the desiccator with different moisture conditions – over the water (humidity ~ 98 %) and oversaturated solution of NaNO₂ (humidity 66 %) [26]. Moisture adsorption results at a humidity of 66 % are presented in Fig. 2 and at 98 % are presented in Fig. 3.

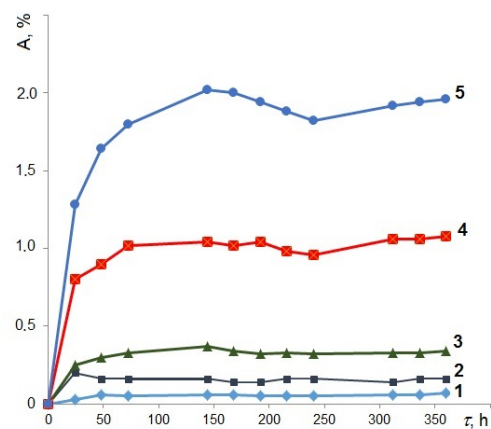


Fig. 2. Dynamic curves of water adsorption by technical grade urea (No. 1) and coated samples (No. 2–5) at 20 °C and humidity ~ 66 %

Gravimetric determination of the moisture adsorption shows that the starch-polymer coating film increases the amount of water adsorbed when relative humidity is 66 %. In comparison, urea without additives under these conditions does not adsorb moisture, and measured mass change is less than 0.1 %. Overall starch-coated samples adsorbed a relatively small amount of moisture with the maximum change in mass at ~ 2 %, which was observed in the 5th sample. It suggests that moisture does not cause deterioration of the fertilizers. Sorption curves of coated granules held over the water at 98 % relative humidity are very similar to those of pure urea. Only an increase in the

amount of adsorbed moisture content is observed with the increasing duration of the process.

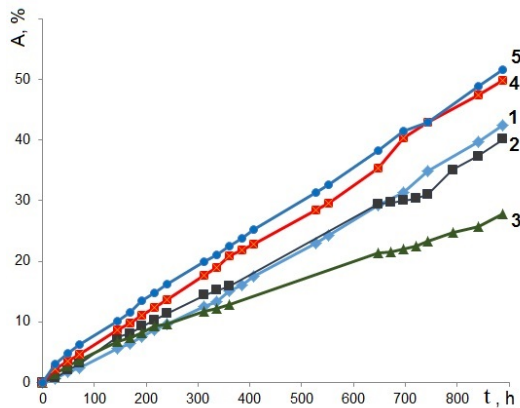


Fig. 3. Dynamic curves of water adsorption by technical grade urea (No. 1) and coated samples (No. 2–5) at 20 °C and humidity ~ 98 %

When the granules are coated only with starch coating substance it reduces permeation of water into the granule (2, 3 samples). However, at higher environmental air humidity fertilizers adsorb more. The obtained results show a correlation between the amount of coating on granules and the adsorbed amount of moisture (water vapour). Granules coated with a single layer of film adsorb almost twice as less water than granules coated with two layers of film.

To evaluate the efficiency of coated urea with starch film, experimental studies of solubility are carried out. Results of solubility tests, calculated as an average of three repetitive experiments, are presented in Fig. 4.

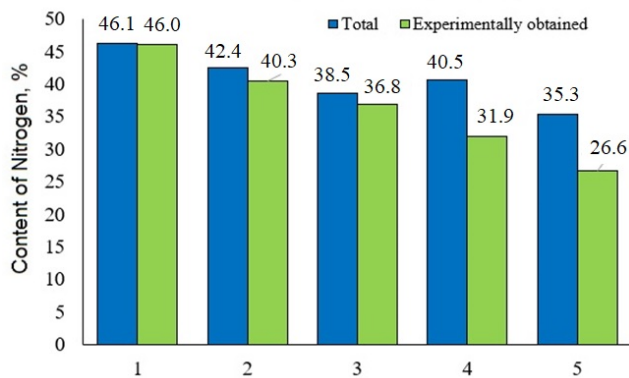


Fig. 4. Results of solubility tests of technical grade urea (No. 1) and coated samples (No. 2–5)

The comparison of the total amide nitrogen content in the granules, and the determined amount of nitrogen after slow dissolution indicates that the potato starch polymer coating with a small amount of dry potato starch protects fertilizer better than a coating of pure polymer. As Fig. 4 shows, the two-layer coating reduces the solubility of fertilizer more than one-layer coating. A double coating of urea with the addition of dry starch filler is more effective. This could be because that the surface is coated more evenly, and not only due to the thickness of the coating itself. The surface of the coated granules (Fig. 5 a) is not smooth, irregularities-surface defects (Fig. 5 b) are visible, which give instability of the solubility results. During the

application of the starch composite coating, control coatings were performed using paint, or the quality of the coating was checked using iodine, which stains the coating layer. Cross-sections of coated urea pellets are shown in Fig. 5 c.

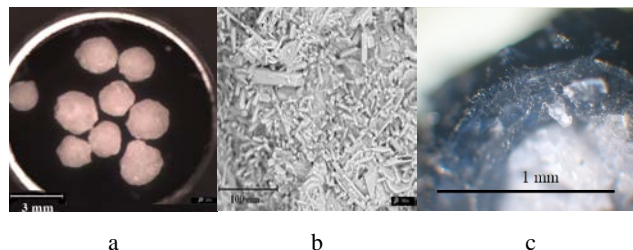


Fig. 5. a – coated urea granules; b – surface SEM photo; c – cross-sections of coated urea pellets

The stability of starch-coated urea granules and the compatibility of the components as well as the resulting stability of the product were verified by instrumental (IR, STA, XRD,) characterization of produced samples. IR spectroscopy results are presented in Fig. 6.

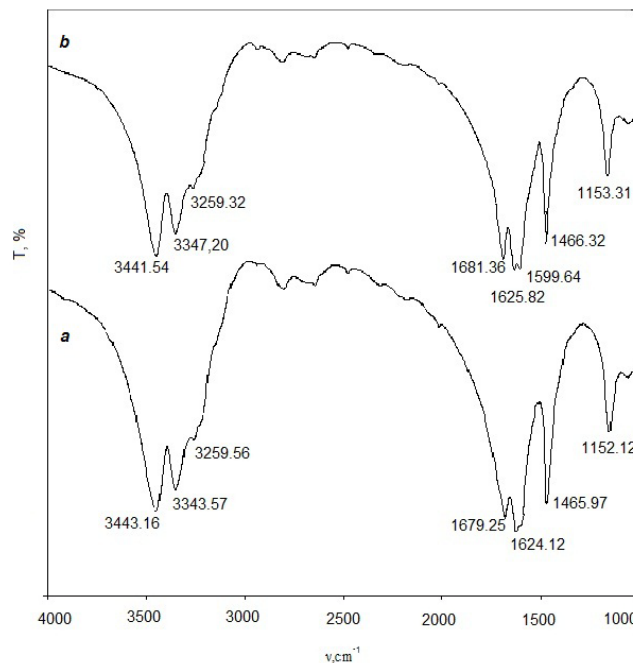


Fig. 6. a – IR spectra of technical grade urea; b – urea coated with two layers of potato starch and dry starch as a filler

IR spectrum of technical grade urea (Fig. 6 a) contains clearly visible absorption bands at 3433 cm^{-1} and 3343 cm^{-1} corresponding to NH_2 group symmetric and asymmetric valence vibrations. The band at 3259 cm^{-1} can also be attributed to the vibrations of the NH_2 group. The next intense absorption band at 1679 cm^{-1} corresponds to the valence vibrations of CO and CN groups and deformational vibrations of the NH_2 group as well as visible band at 1624 cm^{-1} appears because of deformational vibrations of NH_2 and valence vibrations of CN. The band at 1465 cm^{-1} can be attributed to valence vibrations of CN_2 and deformational vibrations of the NH_2 group. The last band at 1153 cm^{-1} appears due to combined vibrations of NH_2 , CN_2 , and CO groups. In comparison, the IR absorption spectrum of urea coated with starch polymer film and dry starch additive contains (Fig. 6 b) contains the same bands that

were attributed to urea. Bands characteristic for starch and starch polymer film should be visible at 1102 cm^{-1} and 1337 cm^{-1} while there is only one band visible at 1153 cm^{-1} corresponding to deformational vibrations of NH_2 group as well as valence vibrations of CN_2 and CO groups [24]. A cross comparison of these two spectra (Fig. 5) clearly indicates that starch film coating with dry starch additive does not change the IR spectrum at all. This might be due to the fact that the amount of coating material is too small and absorption bands of urea mask bands of starch and starch polymer. It is also obvious that during the coating process no new bonds formed as bands of urea remained at the same wavenumber with a slight decrease in their intensity. Overall, no significant change in the IR spectrum of coated urea was observed.

Fig. 7 contains the results of simultaneous thermal analysis of technical grade urea coated with starch film.

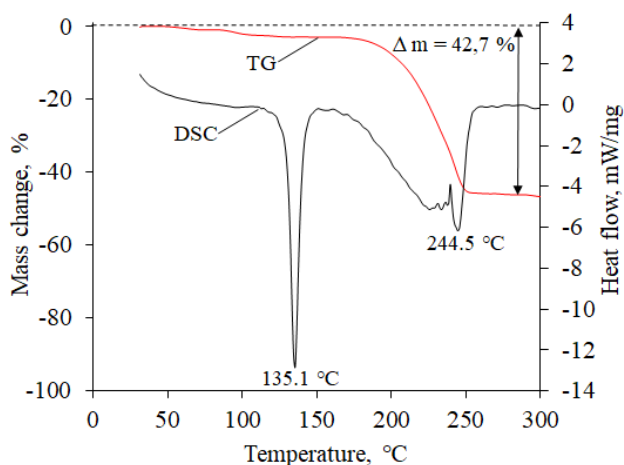


Fig. 7. Simultaneous thermal analysis of urea coated with two layers of potato starch and dry starch as filler

Thermogravimetric and differential scanning calorimetry curves show that decomposition of urea ($\text{CO}(\text{NH}_2)_2$) begins at $\sim 140^\circ\text{C}$ when weight loss is registered.

Endothermic effects characteristic to urea are observed at temperatures of 135.1°C and in the range of $220\text{--}250^\circ\text{C}$. When heated, urea begins to decompose above its melting temperature (132°C) and decomposition take place in three stages: at $190\text{--}260^\circ\text{C}$, $260\text{--}400^\circ\text{C}$, $400\text{--}490^\circ\text{C}$ [27]. STA curves show no significant deviations from theoretical values which proves once more that starch additive does not react with urea and does not form any new compounds, which could influence the thermal resistance of urea. STA curves of coated urea are very similar to thermal analysis results of pure urea.

X-ray diffraction analysis (XRD) results are presented in Fig. 8. Letters K in the diffractogram indicate characteristic peaks of urea which have the highest intensity, because all granules consist mostly of the urea.

All peaks in diffractogram (0.398 ; 0.362 ; 0.304 ; 0.282 ; 0.253 ; 0.242 ; 0.222 ; 0.217 ; 0.199 ; 0.184 and 0.167 nm) are attributable only to urea. Diffraction peaks of starch are not visible because of the low content of starch and its diffraction intensity may be so low, that it does not appear on X-ray diffractogram. Overall no significant change in XRD spectra of starch-coated urea is visible.

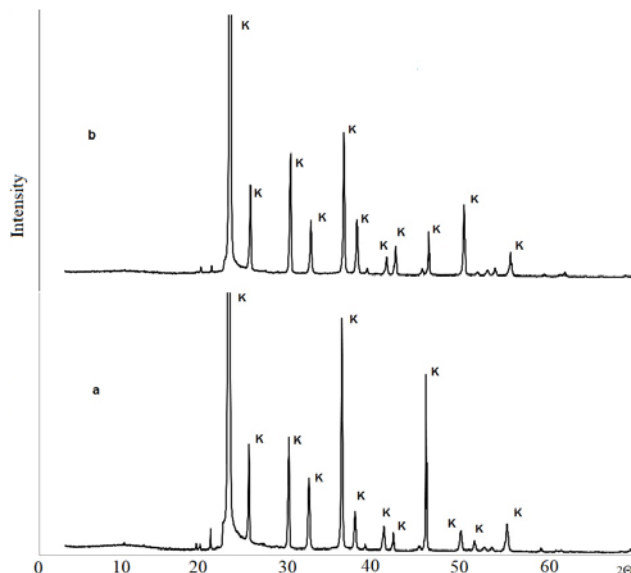


Fig. 8. a – XRD patterns of technical grade urea; b – urea coated with two layers of potato starch and dry starch as filler

4. CONCLUSIONS

This paper reviews the possibilities of starch coating application for the production of slow-release fertilizers. As the component containing nitrogen, urea was used in these experiments. Urea is preferred in the production of slow-release nitrogen fertilizers, because it has the highest content of nitrogen – 46.6 %. During the experiments, starch film was prepared and its stability in different pH values and different salt solutions was evaluated. It was found that the film is sufficiently stable. In that case coating of industrial urea with starch was performed coating. Starch film/coating was evaluated by examining its influence on the properties of fertilizer granules (hygroscopicity and strength). The application of a single layer of starch substance increased static strength of granules up to 22.7 N/gran , while two-layered coating has somewhat reduced granules strength. But their values (19.3 N/gran) are still higher than the minimum requirements provided by fertilizer producers – 7.0 N/gran . The impact of the coating on urea solubility was also estimated. It was found that the mechanical properties of the double coating changes quite insignificantly while coating reduces the solubility of urea by more than 20 %. No chemical interaction between urea and the components used for coating occurred which was confirmed by XRD, STA and IR analyses.

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