

## Controlled-Release NPK Fertilizer Encapsulated by Polymeric Membranes

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The commercial granular fertilizer NPK6-20-30 was coated using polysulfone (PSF), polyacrylonitrile (PAN), and cellulose acetate (CA). The coatings were formed from the polymer solutions by the phase inversion technique. Measurements of the thickness and porosity of the prepared coatings and a microphotographic observation of the coatings were performed. The physical properties of the coatings influence the release rate of macronutrients which are present in the core of the coated fertilizer. In the case of PAN coating with 60.45% porosity, prepared from a 16% polymer solution, 100% of  $\text{NH}_4^+$  and  $\text{P}_2\text{O}_5$  was released after 4 h of test and 99.7% of  $\text{K}^+$  after 5 h of test, whereas in the case of coating with 48.8% porosity, 31.8% of  $\text{NH}_4^+$ , 16.7% of  $\text{P}_2\text{O}_5$ , and 11.6% of  $\text{K}^+$  was released after 5 h. In all experiments, different selectivities of the coatings in terms of the release of components were observed. The release of potassium through the coatings made of PSF and PAN was the slowest. The same tendency was observed for the release of nitrogen through a coating of CA. The release of fertilizer active components was the slowest in the case of PSF. The lowest porosity coating was prepared from the 18% PSF solution.

**KEYWORDS:** Polymer-coated fertilizer; controlled-release fertilizer; slow-release fertilizer

### INTRODUCTION

A major increase in the quantities of agrochemicals used will be necessary to achieve any substantial increase in production of foodstuffs (1). Since the total loss of nutrients, especially nitrogen, supplied as conventional fertilizers is estimated to be from 30% to 50%, depending on the method of application and the soil conditions, the application of these fertilizer is declining (2–4).

One method of reducing nutrient losses involves the use of slow- or controlled-release fertilizers. There are three types of these fertilizers: slightly soluble materials, such as urea–formaldehyde; materials for deep placement, such as urea supergranules; and coated fertilizers. Coated fertilizers are physically prepared by coating granules of conventional fertilizers with various materials that reduce their dissolution rate. The use of controlled-release fertilizers (CRFs) increases their efficiency, reduces nutrient loss and soil toxicity, minimizes the potential for negative effects associated with overdosage, and reduces the frequency of the applications in accordance with normal crop requirements (1, 5, 6).

The physically prepared fertilizers ensure a controlled release of nutrients to the soil by diffusion through the pores or by erosion and the degradation of the coatings (7–9). The release and dissolution rates of water-soluble materials depend on the properties of the coating materials. The materials applied most

frequently as coatings are sulfur, waxes, polyethylene, polystyrene, and kraft pine lignin. Sulfur-coated urea (SCU) has been under development by the Tennessee Valley Authority (TVA) since 1961. Sulfur was selected as a coating material because of its low cost. The first commercial polymer-coated fertilizers were developed by the Arthur Daniels Midland Co. (ADM). The main component of the coating was a copolymer of dicyclopentadiene with a glycol ester (3).

In our previous paper (10), soluble NPK fertilizer was coated with polysulfone to study its reduction of the release rate of macroelements. This work is a continuation of the investigations associated with a new method of CRF production (inversion phase, wet method). We present studies on the possibility of using other polymer materials as a fertilizer coating. The main objective of this research was to evaluate the influence of the types of polymer coatings and their morphology on the release rate of macroelements from CRF granules. Fertilizer coatings prepared from polymers of different degradability (CA > PAN ≥ PSF) were compared.

### MATERIALS AND METHODS

**1. Characteristic of Polymers Used.** The materials used in the preparation of polymer coatings were polysulfone (PSF), cellulose acetate (CA), and polyacrylonitrile (PAN). Cellulose acetate is the classic membrane material used by the pioneers of modern membrane technology to create asymmetric membranes. This polymer is prepared from cellulose by acetylation, i.e., reaction with acetic anhydride, acetic acid, and sulfuric acid. The membranes prepared from CA are hydrophilic; however, they exhibit a low-temperature resistance and

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**Table 1.** Composition of the Polymer Solution for Coating Formation

fertilizer	polymer, wt %	solvent, wt %	modifying agent
NPK6-20-30-PSF	polysulfone, 10–20	DMF, 80–90	none
NPK6-20-30-PAN	polyacrylonitrile, 16–18	DMF, 82–84	none
NPK6-20-30-CA	cellulose acetate, 16–18	acetone, 74–77	formamide

are pH-sensitive. At pH 4–5, their lifetime is about 4 years, whereas at pH 6 they are stable for 2 years. At very basic (pH 9) or very acidic (pH 1) conditions, their lifetime decreases to a few days. CA is highly biodegradable; i.e., it is highly susceptible to microbial attack due to the nature of its cellulose backbone (11).

Polyacrylonitrile is prepared by an acrylonitrile polymerization process. It has a higher temperature resistance than CA, and the membranes prepared from PAN can be used at 318 K and pH from 1 to 10. Moreover, PAN exhibits biological resistance (12).

Polysulfones are ranked second after CA as a commercial membrane material, with applications in both large-scale production and at the laboratory scale. PSF is sulfonated in organic solution using chlorosulfuric acid as the sulfonating agent. PSF is resistant to attack by acids, bases, and salt solutions. The membranes prepared from PSF are resistant to both temperature and pH (13).

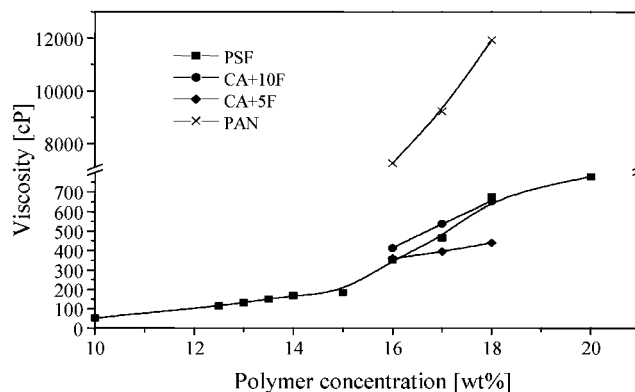
**2. Preparation of the Coated Fertilizer.** Series of fertilizers with different polymer coatings were prepared at a laboratory scale. The mineral fertilizer used for each coating was a commercial water-soluble granular fertilizer, NPK6-20-30, produced by Chemical Plant "Police" S.A. X-ray diffraction analysis showed that the fertilizer contains KCl, NH<sub>4</sub>Cl, and NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>. The diameter of granules used was 3.15 mm.

The coating solutions were prepared by dissolution of the solid polymer in adequate solvent. *N,N*-Dimethylformamide was used for PSF and PAN, whereas acetone was used for CA. The polymer coatings were formed by the phase inversion technique using water as a precipitation bath (10). **Table 1** shows the compositions of polymer solutions applied for the formation of each coating.

The granular fertilizer was gradually added to polymer solution, where it was covered by a thin layer of the solution. The granules were then dropped into the precipitation bath, where the solvent–nonsolvent exchange proceeded, resulting in the formation of coatings (gelation process). The encapsulation process was described earlier (10). The coated granules were removed from water and then dried to a constant mass at elevated temperature. Multiple coatings were prepared by the immersion of the single-coated dried fertilizer granules into polymer solutions. Thereafter the procedure was the same as in the preparation of single-coated fertilizers.

**3. Morphology of Prepared Coatings.** Measurements of the thickness and porosity of the prepared coatings and microphotographic observation of the coatings were performed. The granules were cut, and the thickness of the coatings removed from the granules was measured by a micrometer. The polymer coatings were wetted before porosity measurements. The porosity of the coating was determined by using the gravimetric method, based on the difference in weight between the water-wetted coating and dry coating (dried at 377 K to a constant mass). The method was described previously (10). In the case of coatings prepared from PSF, two types of porosities were estimated due to the hydrophobic character of this polymer. For total porosity determination, the PSF coatings were wetted with alcohol, and then the alcohol was exchanged with water. The effective porosity was determined after immersion of the coating in water. In this case, only part of the pores is wetted. PAN and CA are hydrophilic; thus, their coatings were easily wetted by water and their effective porosity was equal to one.

The coating morphology was examined using a scanning electron microscopy (JEOL JSM-6100). Before the measurement, the coatings were frozen in liquid nitrogen, broken to obtain cross sections, and then coated with a gold layer for SEM observation.

**Figure 1.** Viscosities of polymer solutions at 293 K.

**4. Rate of Release of Active Components in Water.** Coated NPK granules (about 1 g) were placed into five beakers with 50 mL of water, and the amount of nutrients released over time was measured. The uncoated NPK was dissolved after 9 min. The tests were conducted for 5 h, at room temperature. The release rate was estimated as the percentage of the component released after a given time in relation to the initial concentration of this component (10). The P<sub>2</sub>O<sub>5</sub> content of the sample was determined by using the colorimetric vanadate–molybdenum method (14). The color intensity of the yellow complex formed was proportional to the phosphorus concentration. The NH<sub>4</sub><sup>+</sup> and K<sup>+</sup> contents were determined by using the potentiometric method (ORION 920A) using adequate ion-selective electrodes (15).

## RESULTS AND DISCUSSION

The viscosity of polymer solutions affects the coating preparation. Solution viscosities that are too low or too high cause the polymer films coating the granules to be incomplete or damaged. These defects affected the properties of the fertilizer, and the active components were dissolved very quickly and released to water during tests. Solution viscosities were determined by using a Höppler viscosimeter at 293 K. As expected, film-forming solution viscosities increase with an increase in polymer concentration (**Figure 1**). The viscosities of PAN solutions were much higher than those for the other polymers, and therefore encapsulation of fertilizer was performed by using a warm polyacrylonitrile solution ( $T = 333$  K).

It was observed that the solution polymer concentration influences the porosity of the prepared coating. The polymer coating porosity is a crucial parameter. This property limits the diffusion of water into the fertilizer granule and of nutrients out of the granule. The dependence of the porosity of prepared coatings on polymer type and its concentrations in the film-forming solutions is shown in **Figure 2**.

The coatings formed from solutions with a higher polymer concentration exhibited lower porosity, as shown in **Figure 2**. This dependence is associated with the rate of water–solvent exchange in the precipitation bath during film formation. The rate of initial polymer precipitation is higher for solutions with higher polymer concentration. This results in a denser skin layer, which slows the remaining water–solvent exchange. The resulting membrane is more compact and less porous. The effective porosity of single coatings from PSF (the porosity of water-wetted coatings) ranged from 53% to 19.4%. The total porosity of these coatings (the porosity of methanol-wetting coatings) was higher by about 40% (**Figure 3**). This difference was associated with the hydrophobic character of PSF. When the hydrophobic membrane is not wetted with alcohol, the water can penetrate only into the biggest pores of the membrane. Small pores are accessible to water only after wetting of the membrane

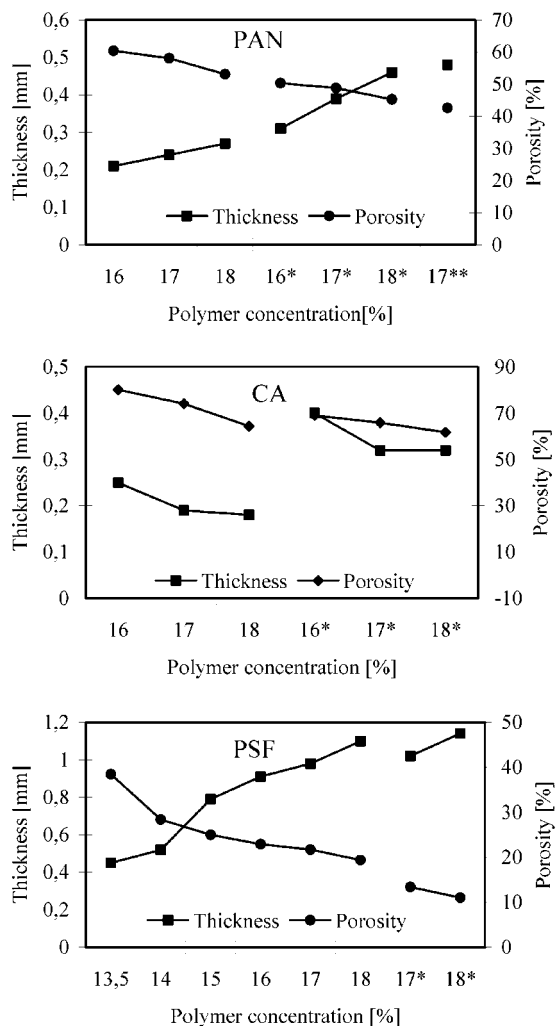


Figure 2. Influence of polymer concentration in film-forming solution on the thickness and porosity of prepared coatings. \*, double coating; \*\*, triple coating

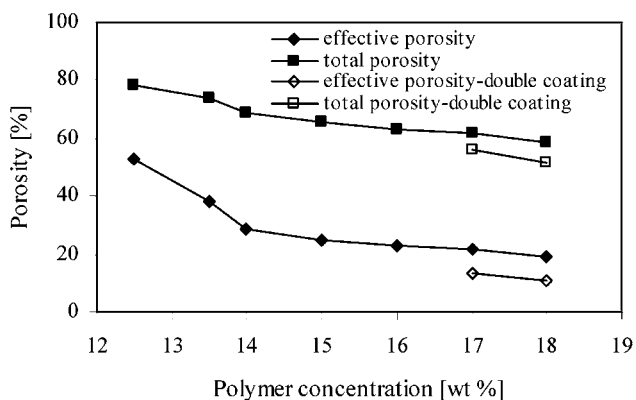


Figure 3. Comparison of total and effective porosity of polysulfone coatings.

with alcohol. Thus, in this case the total porosity does not influence the release rate of fertilizer components. Because the dynamic release tests were performed in water, only the effective porosity determined the transport of water into the coated fertilizer granule and nutrients out of the granule. The porosity of CA single coatings was in the range from 88.5% to 64.5%, whereas for PAN single coatings the porosity ranged from 60.4% to 53.1%.

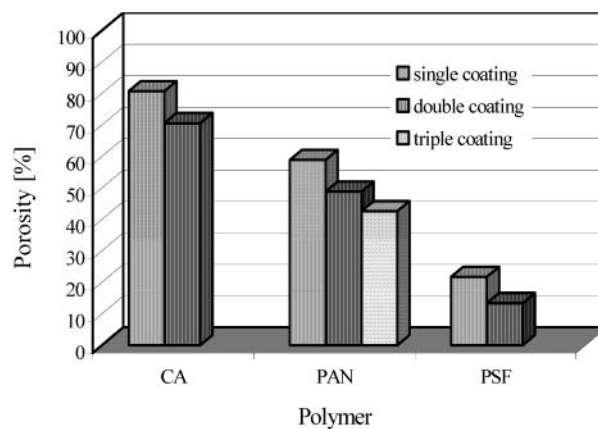


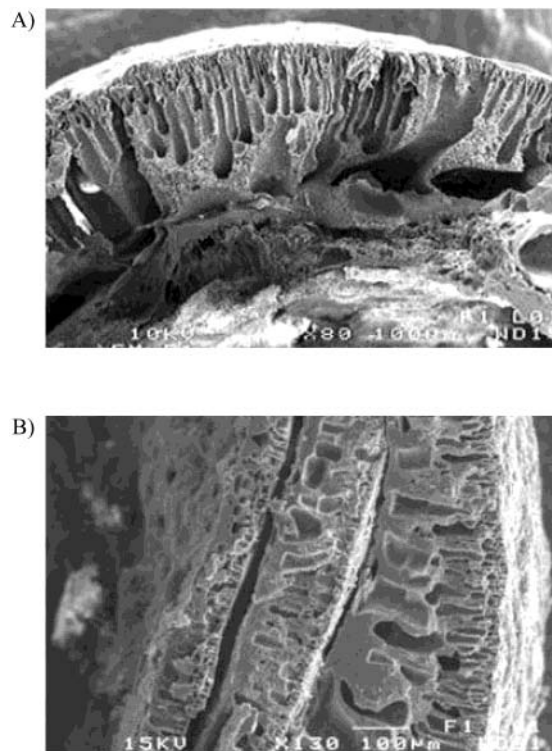
Figure 4. Dependence of prepared coatings' porosity on the number of polymer layers. The coatings were prepared from solutions containing 18% of CA with 5 wt % of formamide, 17% of PAN, and 18 wt % of PSF, respectively.

During the subsequent coating of pre-coated granules of fertilizer, it was observed that the first layer slightly dissolved. As a consequence, the porosity of multiple coatings was much lower than that of a single coating. For example, the porosity of double coatings (fertilizer designated \*) prepared from 17% and 18% PSF solutions decreased by about 8% and resulted in effective porosities of 13.4% and 11.0%, respectively (Figure 3). The dependence of coating porosity on the number of polymer layers forming the coating is shown in Figure 4. Taking into account their initial porosity, the changes in porosity of double- and triple-layer coatings prepared from CA and PAN were similar to that of PSF, but they had effective porosities of 63.6% and 42.6%, respectively.

In the case of coatings prepared from CA, the amount of formamide added to the polymer solution also influences the coating porosity. Higher amounts of formamide increased the coating porosity. For example, the porosity of the coating prepared from 18% CA solution with 10% of formamide was 71%, whereas with 5% formamide addition it was 64.4%.

The average thickness of fertilizer coatings is presented in Figure 2. The results show that, for coatings prepared from PSF, the thicknesses significantly depended on the polymer concentration in the casting solutions and were in the range from 0.45 to 1.1 mm. A slight dissolution of the first layer, as mentioned earlier, could be the reason that the thickness of a double-layer coating was nearly the same as that of a single-layer coating. The coating prepared from solution with a higher polymer concentration exhibited a large thickness, due to the higher viscosity of the coating solution, leading to a thicker layer of the polymer covering the granule. Coatings prepared from PAN and CA had thicknesses much smaller than the PSF coatings. Moreover, in the case of CA, the thickness even decreases slightly with an increase of polymer concentration in the film-forming solution.

The microscopic structures of the fertilizer coatings, obtained by using scanning electron microscopy, are shown in Figure 5. The prepared coatings in all cases are asymmetric, with a clearly outlined thin skin layer. The skin acts as a barrier which reduces the rate of intragranular diffusion of water, the dissolution of ingredients, and fertilizer transfer out of the granule. Figure 5A presents a cross section of double coating prepared from a 16% solution of CA. As can be observed, the second layer caused damage and a slight dissolution of the first coat. The border between them is difficult to observe. In the case of triple coating prepared from a 17% solution of PAN, the borders

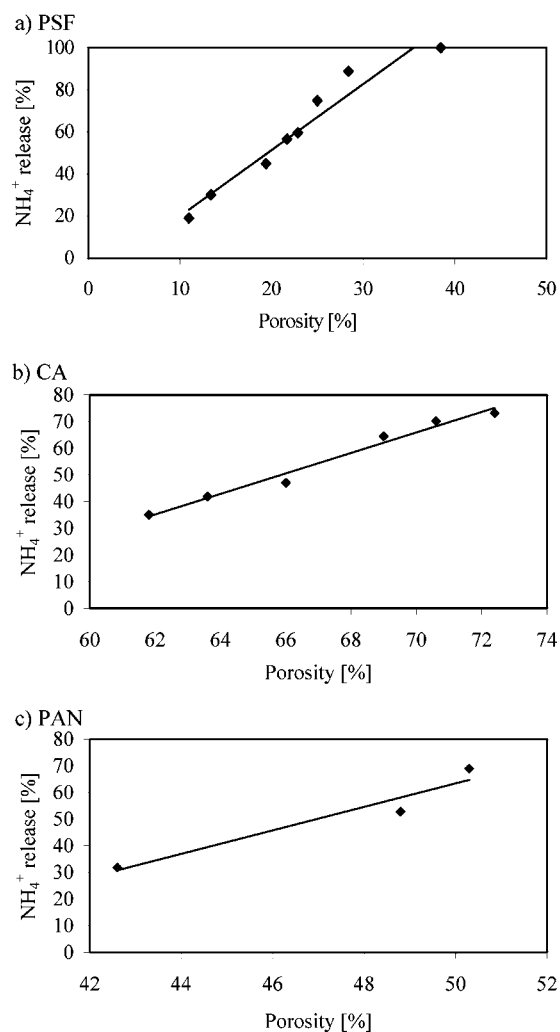


**Figure 5.** SEM of cross section of coatings: (A) NPK6-20-30CA16+5%F\*, (B) NPK6-20-30PAN17\*\*.

are visible (**Figure 5B**). The layers do not damage the preceding layer. The coating comprises three films, and each film is asymmetric with a skin layer. The lower layer has cylindrical elongated, finger-type macropores. The double coating prepared from a solution of PSF has no border between the first and second layers (10). This absence of a border was associated with the fact that, during the subsequent coating of pre-coated granules of fertilizer, the first skin layer was dissolved (dissolution was larger than in the case of cellulose acetate). However, the outer skin layer was more compact and denser.

Dynamic tests to assess the fertilizer release rate of the active components through a polymer coating showed that the release rate was a function of the coating structure and can be controlled by adjusting the thickness and porosity of the coating. The mechanism of macronutrients release from encapsulated granule was discussed earlier (10). The studies demonstrated that the release rate of N, P, and K from coated granules decreases with increasing polymer concentration in the solution used for coating formation. This may be due to the fact that the structure of the coating was denser when a more concentrated polymer solution was used. For each type of polymer coating tested, the slowest release of the ingredients was observed in the case of the granules with the smallest porosity. It was also observed that the release rate of components is affected by both the porosity and the type of polymer used for coating preparation. **Figure 6** demonstrates the influence of polymer coating porosity on the release rate of  $\text{NH}_4^+$ . In the case of coatings prepared from CA and PAN, only the results obtained for multiple coatings are presented, because for single coatings 100% of  $\text{NH}_4^+$  was released after 5 h of test (independent of the porosity).

In addition, the effect of multiple coatings of the fertilizer granules on the release of macroelements was studied. The double- or triple (in case of PAN)-layer coatings caused the ingredients to be released at a slower rate. For example, in the case of sample NPK6-20-30 PAN 17 (single coating prepared from 17% PAN solution), after 5 h, 93.7% of  $\text{K}^+$  was released,

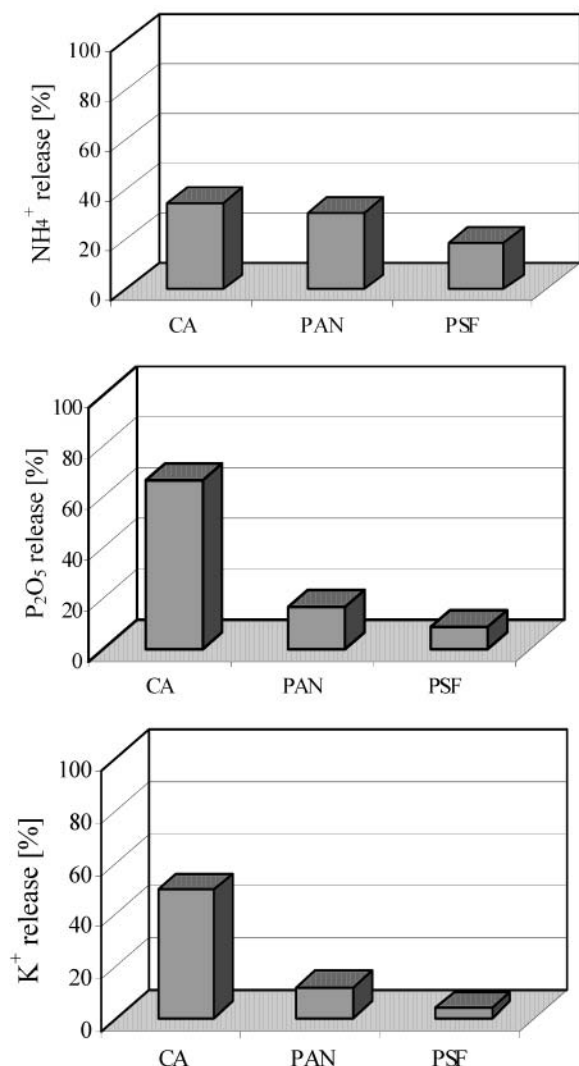


**Figure 6.** Influence of polymer coating porosity on the release of  $\text{NH}_4^+$  after 5 h of dynamic tests.

whereas in the case of NPK6-20-30 PAN17\*\* (triple coating prepared from 17% PAN solution), only 11.7% of  $\text{K}^+$  was released. The reduction of the multicoated granules' release rate was caused by a more compact structure of the coating and a lower porosity in comparison with that for the single coating.

The effect of polymer type used for coating preparation on the release of components after 5 h of dynamic test is shown in **Figure 7**. A comparison was made between polymer coatings which exhibited the most favorable properties, i.e., those which released the smallest quantity of nutrients. In the case of PSF, it was the fertilizer double-coated with 18% polymer solution. For fertilizer with CA coating, the slowest release of macroelements was achieved with a double coating from an 18% polymer solution with 5% formamide in the casting solution. For PAN it was achieved with a triple coating from a 17% solution of polymer.

It was observed that the ingredients from fertilizer with CA coating were released most rapidly. After 5 h of test, 66.5% of  $\text{P}_2\text{O}_5$ , 49.6% of  $\text{K}^+$ , and 35% of  $\text{NH}_4^+$  was released. The ingredients from granules with a double coating prepared from 18 wt % PSF solution had the lowest release rate. It was found that 19.0% of  $\text{NH}_4^+$ , 8.7% of  $\text{P}_2\text{O}_5$ , and 3.8% of  $\text{K}^+$  was released after 5 h. The differences in the release rates of active components can be associated with both the porous structure of the coating and the nature of the coating material. The slowest release of active components through PSF coating is associated



**Figure 7.** Influence of polymer type used for coating formation on the release of active components (release for the most compact coatings, NPK6-20-3-CA18+5%F\*, NPK6-20-30PAN17\*\*, and NPK6-20-30PSF18\*).

with the hydrophobic character of the polymer. The contact angle for PSF was determined to be 80°, for PAN it was 58°, and for CA it was 68°. The higher the value of the contact angle, the more hydrophobic the layer. Thus, the wettability of the polysulfone membrane, i.e., the penetration of water through the membrane pores, is more difficult than that through the hydrophilic coating formed from PAN or CA. The smaller the amount of water that diffuses through the coating into the fertilizer core, the lower the release rate of macroelements out of the granules. Moreover, the coatings prepared from CA, PAN, and PSF act as selective barriers to the components, which therefore were released at different rates. In the case of coatings made from PSF and PAN, the NH<sub>4</sub><sup>+</sup> ions were released most rapidly, whereas the release of K<sup>+</sup> ions was the slowest. In contrast, in the case of CA coating, the phosphorus ions were released most rapidly and NH<sub>4</sub><sup>+</sup> ions were released most slowly.

These studies show that the hydrophobic/hydrophilic character of the material used in the preparation of the coating has a substantial influence on the nutrient release. For example, comparison of coatings prepared from PAN and PSF showed

that the release rate of NH<sub>4</sub><sup>+</sup> is 3 times faster in the case of hydrophilic coatings (PAN), although the total porosity of the coatings was the same.

It was observed that the release rate of components from the fertilizer coated with biodegradable coating (CA) was the highest. In the case of coatings prepared from PAN and PSF, the release rate of nutrients was much lower. These coatings are not biodegradable, but their presence in soil can improve the soil structure and quality.

The tests showed that the phase inversion technique can be used for preparation of CRF fertilizer. The time of the fertilizer release can be controlled by the type of polymer used and by the parameters of the coating formation.

#### LITERATURE CITED

- (1) Akelah, A. Novel utilizations of conventional agrochemicals by controlled release formulations. *Mater. Sci. Eng.* **1996**, *C4*, 83–98.
- (2) Winiarski, A. Methods of increasing of nitrogen utilization from mineral fertilizer associated with the fertilizer production and application. *Pr. Nauk. Politech. Wroclaw* **1994**, *22*, 116–123 (in Polish).
- (3) Salman Omar, A. Polyethylene-coated urea. Improved storage and handling properties. *Ind. Eng. Chem. Res.* **1989**, *28*, 630–632.
- (4) Salman Omar, A.; Hovakeemian, J.; Khraishi, N. Polyethylene-coated urea. 2. Urea release as affected by coating material, soil type and temperature. *Ind. Eng. Chem. Res.* **1989**, *28*, 633–638.
- (5) Pipko, G.; Maugor, S. Method for manufacture of slow-release fertilizers. European Patent EP 0276179, 1998.
- (6) Al-Zahrani, S. Utilization of polyethylene and paraffin waxes as controlled delivery systems for different fertilizers. *Ind. Eng. Chem. Res.* **2000**, *39*, 367–371.
- (7) El-Refaie, K.; Al-Sakran, A. Controlled release formulations of agrochemicals from calcium alginate. *Ind. Eng. Chem. Res.* **1996**, *35*, 3726–3729.
- (8) Heulaly, F. M.; Abdel-Bary, E. M.; Sahran, A. A. Minimalization of water pollution and environmental problems via controlled release styrene butadiene rubber formulations containing ammonium nitrate. *Plast., Rubber Compos. Process. Appl.* **1993**, *19*, 111–115.
- (9) Byung-Su, K.; Young-Sang, C.; Hyun-Ku, H. Controlled release of urea from rosin-coated fertilizer particles. *Ind. Eng. Chem. Res.* **1996**, *35*, 250–257.
- (10) Tomaszewska, M.; Jarosiewicz, A. Use of polysulfone in controlled-release NPK fertilizer formulations. *J. Agric. Food Chem.* **2002**, *50*, 4634–4639.
- (11) Cheryan, M. *Ultrafiltration and Microfiltration Handbook*; Technomic Publishing Co.: Lancaster, PA, 1998.
- (12) Bodzek, M. Ultrafiltration Membranes from Polyacrylonitrile. *Polimery (Warsaw)* **1984**, *29*, 63–66 (in Polish).
- (13) Staude, E.; Breitbach, L. Polysulfones and their derivatives: Materials for different separation operations. *J. Appl. Polym. Sci.* **1991**, *43*, 559–565.
- (14) Maćkowska, E.; Gogolin, R. *Inorganic Quantitative Analysis*; Technical Agriculture Academy: Bydgoszcz, 1999 (in Polish).
- (15) Benrhop PH/ISE Meters, Model 720 A, Instruction Manual.

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