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BIODEGRADABLE POLYMER COMPOSITES WITH NITROGEN- AND PHOSPHORUS-CONTAINING WASTE MATERIALS AS THE FILLERS

BIODEGRADOWALNE KOMPOZYTY POLIMEROWE WYPEŁNIONE ODPADAMI ZAWIERAJĄCYMI AZOT I FOSFOR

Abstract: Composites consisting of polyvinyl alcohol, nitrogen- and phosphorus-containing waste materials were prepared and studied as materials for encapsulation of mineral fertilizers. By-products of biodiesel production (rapeseed cake, crude glycerol), horn meal (waste product of haberdashery) and phosphogypsum (by-product of the production of phosphorus fertilizers) were used as the fillers of the composites. The films of the composites with the different amounts of nitrogen and phosphorus were prepared using different fillers or their mixtures. Mechanical, properties of the films, hygroscopicity, solubility in water were studied. The composites developed were used for the encapsulation of mineral fertilizers. It was established that encapsulation resulted in the increase of the time of release of the fertilizers. The developed slow-release fertilizers represent a combination of inorganic and organic compounds. The organic part consists of nitrogen- and phosphorus containing horn meal and rapeseed cake. Since assimilation of organic substances is considerably longer, nitrogen and phosphorus of these components will be available for plants much later than inorganic nitrogen and phosphorus. Thus the composite film will not only decrease the rate of desorption of the components from the granules of the fertilizers but will also prolong the impact of the fertilizers on the plants.

Keywords: composites, rapeseed cake, horn meal, fertilizer, encapsulation, slow-release

Introduction

The problem of utilization of waste materials which are formed in agriculture, processing industry and in other sectors of economy recently becomes increasingly urgent. Keratin-containing waste materials such as animal hair, hoofs, horns, feather of birds represent one kind of such wastes. Such wastes can cause certain environmental problems. On the other hand they can be used as raw materials for the production of valuable products. For example, keratin-containing wastes can be used for the production of haberdashery goods. They can also be used as a source of proteins. A method of manufacturing fibrous

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keratin-containing composite materials by wet spinning was reported [1]. For the preparation of such composites natural polymers, *ie* biomodified cellulose and keratin obtained from chicken feather were used. Keratin is insoluble in water and in dilute solutions of alkalis and salts. For this reason its isolation and recovery requires complex technologies consisting of many stages of chemical treatment [2]. The search for the simpler methods of the application or processing of the keratin-containing waste materials is currently in progress. For example, extrusion of the mixture of feather, glycerol and sodium sulphate was reported [3]. The films prepared by pressing of the triturated feather and glycerol were reported to be useful as mulch and as packaging materials [4]. Since keratin contains 15-18% of nitrogen and 1.5-2% of phosphorus, keratin-containing waste materials can be used as fertilizers [5, 6]. Materials of vegetal origin, such as coarse meals of yellow and white lupin seeds, waste products of corn processing, coarse meal of castor cake can also be used for fertilization of plants [7]. Since nitrogen and phosphorus exist in these materials as components of organic compounds the plants cannot assimilate them directly. The organic fertilizers first have to be decomposed into inorganic compounds. For this reason the process of assimilation of organic fertilizers is considerably longer than that of inorganic ones. Fertilization with readily dissolving inorganic fertilizers is associated with great losses and contamination of water and environment since plants do not manage to fully assimilate them. Production of the slow-release fertilizers enables to avoid this problem. Such fertilizers can be obtained by several methods. One method is based on the coating of the granules of fertilizers with the films which reduce the rate of desorption of nutrients and reduces soil toxicity and nutrient loss, minimizes the potential negative effects associated with the over dosage. Both inorganic and organic compounds are used for the coatings [8-11]. Organic compounds are applied in the form of polymeric emulsions and solutions. For example, the mixture of starch and acrylic acid was reported to be useful for the encapsulation of carbamide [12]. For the encapsulation of the fertilizers consisting of $\text{NH}_4\text{H}_2\text{PO}_4$, NH_4Cl and KCl the mixture of polysulfone and starch was proposed [13]. The encapsulated fertilizers possess improved mechanical and physical properties as compared with the non-encapsulated analogues. They exhibit lower hygroscopicity. They do not clump during storage. Variation of the thickness of the coatings enables to control the release of the nutrients subject to the period of vegetation of plants.

The permeability to water vapours and fertilizer depends on the properties of a polymer used [14]. Polymers, the role of which is to decrease the rate of release of nutrients, can be used not only for coating of fertilizers but also for the preparation of the mixtures of fertilizers and polymer particles which are known as the slow-release fertilizers [15, 16]. Commercially available fertilizers Nutricote® (Chisso-Asahi Fertilizer Company, Ltd, Tokyo, Japan) employs thermoplastic polymers such as polyolefins, poly(vinylidene chloride), and copolymers as coating materials. The coating process involves coating of a soluble fertilizer core with a thermoset copolymer of dicyclopentadiene and a glycerol ester dissolved in an aliphatic hydrocarbon solvent. For the fabrication the slow-release fertilizers Polyon® Pursell Industries employed a reactive layer coating process in which two reactive monomers applied to the fertilizer substrate are subjected to step-growth polymerization in a continuous coating drum, forming an ultra-thin polyurethane membrane coating [17]. The slow-release fertilizers prepared using synthetic polymers have one serious shortcoming related to the environmental problems. After release of the nutrients the residues of polymers remain in soil for a long time.

Great potential in the production of the slow-release fertilizers is associated with the application of organic waste materials. Organic waste materials can be used for the preparation of cheap, biodegradable films and granules, which decompose in the soil into useful nutrients. Roh et al reported on application plastic pellets containing feather fibers for the enhancement of growth and flowering of Begonia [18]. Starch, soy protein, polylactic acid, polyvinyl alcohol (PVA) are usually used as the binders in composites while vegetal wastes such as banana fiber, palm leaf, peanut husks, sago pith or agro-industrial waste such as lignocellulosic fibers, by-products, derived from sugar cane, apple and orange fruit juice extraction wastes are used as the fillers [19-24].

The aim of this work was preparation of film-forming composites from PVA and waste materials such as horn meal, crude glycerol, rapeseed cake, phosphogypsum and investigation of their properties and of the applicability for the encapsulation of mineral fertilizers. Since the granules of slow-release fertilizers are coated with the biodegradable films containing nitrogen and phosphorus the degradation of which in soil results in the formation of additional nutrients for plants the synergistic effect is expected to be achieved using such fertilizers. To our knowledge horn meal, rapeseed cakes have not yet been used for the preparation of the coatings for the slow-release fertilizers.

Materials and methods

Materials

Polyvinyl alcohol JF-17 (Kuraray America Inc. and Japan Vam and Poval, hydrolysis degree 98.0-99.0%, viscosity 28-32 MPa) was used as a polymer binder in the preparation of the composites. Crude glycerol and rapeseed cake were obtained from the biodiesel company "Mestilla" (Lithuania). The defatted rapeseed cake was grinded and screened with the sieve the diameter of mesh of which was 0.16 mm before use. Phosphogypsum was obtained from the company "Lifosa" (Lithuania). Horn meal was obtained from the private company producing haberdashery goods. Fine fraction of horn meal with the particle size ≤ 0.16 mm was used. Table 1 shows the amounts of nitrogen and mobile phosphorus in the components used for the preparation of composites.

Table 1
The concentration of nitrogen and mobile phosphorus in horn meal, rapeseed cake, phosphogypsum and crude glycerol

Content	Horn meal	Rapeseed cake	Phosphogypsum	Crude glycerol
N [%]	13.4	7.1	-	-
P [%]	0.27	0.075	0.118	0.15

Ammonium acetate, acetic acid, lactic acid, sulphuric acid, potassium sulphate, copper sulphate were purchased from Lach-Ner (Czech Republic). Granulated mineral fertilizers (single superphosphate) were purchased in the local market.

Sample preparation

Compositions of the mixtures used for the preparation of composite films are given in Table 2.

Table 2

Compositions of the mixtures used for the preparation of the composites

Component amount in the mixture [g] [*]					
Sample	PVA	Horn meal	Rapeseed cake	Phosphogypsum	Crude glycerol
1	4	6	0	0	3
2	4	4	2	0	3
3	4	2	4	0	3
4	4	0	6	0	3
5	4	4	0	2	3
6	4	2	0	4	3
7	4	0	0	6	3
8	4	0	4	2	3
9	4	0	2	4	3
10	10	0	0	0	3

* Water up to 100 g

The mixtures of crude glycerol and PVA were heated while stirring up to 85°C during 15-20 min and stirred at this temperature for another 10 min. Then the rest of components were added and stirred for another 30 min. The films were casted from the hot composite mixtures on polypropylene Petri dishes and dried in a ventilated oven at 25°C for 48 h. The dried films were removed from the casting surface and stored at ambient temperature (23±2°C) and at 50% relative humidity (RH) in a desiccator containing saturated solution of calcium nitrate.

Mechanical testing

Tensile tests were performed using a ZWICK/ROELL BDO-FBO.5TH testing machine with a crosshead speed of 10 mm/min. The test samples were of 45 mm length, and of 5 mm width. Their thickness was measured with a digital micrometer (MEGA Dobry Wybor, Poland). The presented values are the average of at least 5 measurements.

Hardness

The hardness of films was measured with a Hepler consistometer by pressing a cylinder steel pin with the diameter of the bottom of 5 mm into the specimen under a load of 750 g for 60 s. The arithmetic average of the hardness of three film samples (thickness 0.20-0.22 mm) was taken. The hardness of films was calculated by following equations:

$$H = \frac{S}{F} = \frac{4 \cdot G}{\pi \cdot \Delta h^2} \quad (1)$$

where H is the hardness of specimen [N/mm²]; G is the real force acting on a specimen [N].

$$S = \frac{\pi \cdot \Delta h^2}{4} \quad (2)$$

where S is the contact surface of the specimen [mm²]; Δh^2 is the square value of the difference between readings of the micro indicator when sample is unloaded and under load [mm²].

Density

Film samples were dried in a desiccator with silica gel for 1 week and weighed with the accuracy of 0.0001 g. Density of the films were calculated by following equations:

$$\rho = \frac{m}{A \cdot \delta} \quad (3)$$

where ρ is the density of the film [g/cm^3]; m is the mass of the film; A is the film area [cm^2] and δ the film thickness [cm].

The data were averages of 5 measurements.

Film solubility

Film samples (2x2 cm) were dried in a desiccator with silica gel for 1 week and weighed with the accuracy of 0.0001 g (m_0). For the estimation of solubility they were placed into the glass vessel with the distilled water and kept at $20 \pm 2^\circ\text{C}$ for 24 h. Then the samples were taken out and dried at the beginning at the room temperature and later in a desiccator with silica gel for 1 week. After the drying the samples were weighed (m). The solubility in water S [%] was calculated by the equation:

$$S = \frac{m_0 - m}{m_0} \cdot 100 \quad (4)$$

The data were averages of 5 measurements.

Moisture absorption

To determine moisture absorption, samples were dried in a desiccator with silica gel at $20 \pm 1^\circ\text{C}$ for 1 week and weighed with the accuracy of 0.0001 g (m_0). Then, they were conditioned in a container at 100% relative humidity at $20 \pm 1^\circ\text{C}$. They were then removed at certain time intervals, gently blotted with tissue paper to remove excess water on the surface and then were weighed (m_1). The moisture absorption [%] was calculated by the equation:

$$MA = \frac{m_1 - m_0}{m_0} \cdot 100 \quad (5)$$

The data were averages of 5 measurements.

Estimation of nitrogen and phosphorus

The amount of nitrogen in composites was estimated by Kjeldahl method. Mobile compounds of phosphorus were determined by Egner-Riem-Domingo method (AL-method). The phosphorus compounds were extracted from the films with the solution consisting of 77 ± 0.1 g ammonium acetate dissolved in 500 cm^3 of distilled waters, 175 cm^3 of acetic acid and 1 mol of lactic acid. The extractants were analyzed by the molybdenum-blue method with a spectrophotometer Lambda 25 UV/VIS (Perkin Elmer) to determine concentration of phosphorus in the solutions.

Estimation of the rate of dissolution of fertilizers

100 cm^3 of distilled water was poured on the certain amount of encapsulated fertilizers and the electrical conductivity was measured at the definite periods of time. The electrical

conductivities of solutions were measured at 25°C using a conductometer inoLab Cond 730. The data were averages of 3 measurements.

Results and discussion

Composites were prepared from PVA and from different waste materials containing phosphorus and nitrogen. PVA was used as a binder, rapeseed cake (the by-product of biodiesel production), horn meal (the waste product of haberdashery), phosphogypsum (the by-product of production of phosphorus fertilizers) were used as the fillers and the crude glycerol (the by-product of biodiesel production) was used as the plasticizer. Phosphogypsum is used in agriculture as a fertilizer and as additive of soil improving its quality [25, 26]. It contains phosphorus derivatives the amount of which depends on the composition of phosphate rocks used for the production of the fertilizers and can vary in a wide range. The amounts of PVA and glycerol in the composites prepared in this work were constant. The mass ratio of PVA and fillers was 4:6 (Table 2).

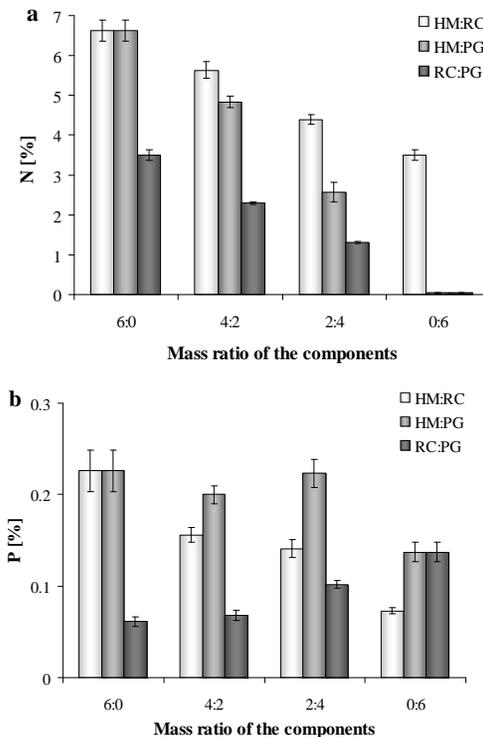


Fig. 1. The dependence of nitrogen (a) and phosphorus (b) content on the mass ratio of the filler components in the films of the composites. Mass ratio PVA:filler = 4:6

The films of the composites with the different amounts of nitrogen and phosphorus were prepared using different fillers or their mixtures. Figure 1 show dependencies of the

concentrations of nitrogen and phosphorus in the composites on the mass ratio of the components. The different mass ratios of horn meal and rapeseed cake (HM:RC), horn meal and phosphogypsum (HM:PG), rapeseed cake and phosphogypsum (RC:PG) were used. With the change of the mass ratio of HM and RC from 6:0 to 0:6 the concentration of nitrogen in the composites changed from 6.6 to 3.5%. Replacement of a part of rapeseed cake or horn meal with phosphogypsum lead to the considerable decrease of the concentration of nitrogen in the composites. The content of phosphorus exhibited more complex dependence on the mass ratio of the active fillers. With the change of mass ratios HM:RC and HM:FG in a series 6:0, 2:4, 4:2, 0:6 it decreased from 0.23 to 0.07%, and from 0.23 to 0.14% respectively. For the composites prepared using the mixtures of rapeseed cake and phosphogypsum it increased from 0.06 to 0.14% with the change of mass ratio of RC and PG from 6:0 to 0:6. It follows from the data presented that the selection of the different fillers enables to obtain the coatings for the granules of fertilizers containing the different amounts of nutrients. Such coatings can be useful from the different points of view. They decrease the rate of desorption of the nutrient compounds from the granules of fertilizers and thus prevent their losses and contamination of the environment. The organic compounds present in the coatings and the products of their degradation stimulate development of microorganisms and enhance their variety.

Table 3 shows the results of the studies of mechanical properties of the films of the composites. The films in which the mass ratios PVA:HM, PVA:RC and PVA:PG were 4:6 exhibited the tensile strength of 10.2, 14.0 and 4.95 MPa respectively. Elongation at break of the same series of films was found to be 5.58, 4.14, 121% respectively while the tensile modulus was 442, 432 and 152 MPa correspondingly. Thus the films of the composites containing phosphogypsum exhibit enhanced elasticity as compared to the composite films filled with horn meal and rapeseed cake.

Table 3

Mechanical properties of the films of composites

Mass ratio of the components	Tensile strength [MPa]	Elongation at break [%]	Tensile modulus [MPa]
PVA:HM:RC			
4:6:0	10.2±0.6	5.58±0.44	442±22
4:4:2	11.3±0.5	3.45±0.41	345±24
4:2:4	11.0±0.6	4.62±0.40	325±16
4:0:6	14.0±0.8	4.14±0.20	432±21
PVA:HM:PG			
4:4:2	10.2±0.1	7.01±0.65	454±26
4:2:4	7.41±0.30	79.0±6.9	249±16
4:0:6	4.95±0.28	121±8	152±7
PVA:RC:PG			
4:4:2	12.1±0.6	6.13±0.52	539±25
4:2:4	6.64±0.24	30.9±2	328±14
10:0:0	35.4±3.8	262±18	216±8

Elasticity is an important property characterizing the applicability of composites for the formation of coatings. Elastic coatings are more resistant with respect of mechanical action than the brittle ones. Only uniform films having no cracks can be used for encapsulation of fertilizers. The effect of phosphogypsum on the mechanical properties of the composite films

was found to be different when it was used in combination with horn meals and with rapeseed cake. The changes of the mass ratios HM:PG and RC:PG in the composite films from 6:0 to 2:4 resulted in the decrease of the tensile strength of the films of the composites containing HM and PG by 27.3%, and of the composites containing RC and PG by 52.7%. Elongation at break in such case increased by 14.2 and 7.5 times respectively. The mass ratio of HM and RC in the composites had no substantial influence to the mechanical properties of the films.

The hardness values of the composite films filled with the mixture of HM and PG and with the mixture of RC and PG measured by Hepler consistometer are given in Figure 2.

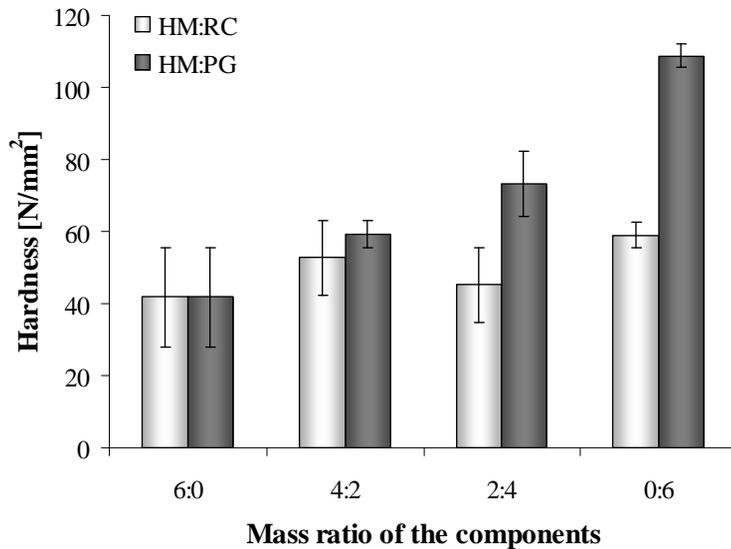


Fig. 2. The dependence of the hardness of the composite films on the mass ratio of the filler components. Mass ratio PVA:filler = 4:6

The hardness of the films of PVA containing no fillers was found to be 218 N/mm² (Table 1, Sample 10). The hardness of the films of the composites containing horn meals and rapeseed cake was found to be *ca* 5 times lower and almost did not depend on the mass ratio of HM and RC. The composite films containing phosphogypsum were found to be harder and their hardness increased with the increase of the content of PG. This observation can be explained by the increase of the density of the composite films with the increase of the content of PG (Table 4). The change of the mass ratio of HM and PG from 6:0 to 0:6 resulted in the gradual increase of the density of the composites from 0.76 to 1.05 g/cm³ and in the increase of hardness from 41.8 to 109 N/mm².

Films which are used for coating of fertilizer particles act as physical barriers that control the nutrients release. For this reason solubility and hygroscopicity of such films are important factors which predetermine water diffusion rate to a granule inwards and minerals solution outwards. Figure 3 illustrates the solubility of the studied composite films in water.

The solubility of the films of the composites with the mass ratios PVA:HM, PVA:RC and PVA:PG of 4:6 was 32, 46 and 61% respectively while the solubility of the films of PVA without fillers at the same conditions was found to be 63%. The lowest solubility was observed for the composites containing HM, while the highest one was demonstrated by the composites containing PG. The increase of the amount of PG in the composite films resulted in the increase of the solubility.

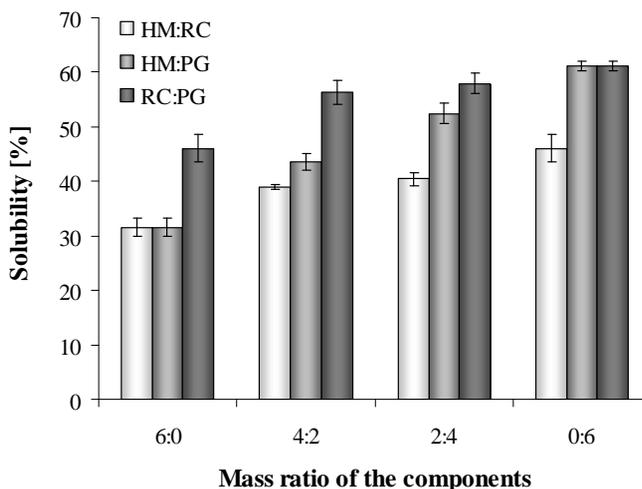


Fig. 3. The dependence of the solubility of the composite films on the mass ratio of the filler components. Mass ratio PVA:filler = 4:6

Figure 4 shows moisture absorption dynamics of the composite films at 20°C and at the relative humidity of 100%. Hygroscopicity of the composite films decreased with the increase of the concentration of PG. At the mass ratio of PVA:PG of 4:6 the moisture absorption of the composite after 10 days was found to be 21%, while that of PVA was 58%. The moisture absorption of the composites reached the limit values within 4-6 days, while film of PVA absorbed water vapour during all the period of experiment (14 days). The ratio of HM and RC did not have any substantial effect on the hygroscopicity of the composite films. These results are consistent with those obtained by Han et al [11]. They have studied the blends of starch and PVA as coatings for the soluble granular fertilizers and established that the sorptive properties of the films depend on the amount of PVA in the blends. Water absorbency of the films increased along with PVA content. The dependence of the physical properties of the coatings of the granular fertilizers on the nature of polymer and on its concentration was also reported by the other authors [10].

Release of nutrients from the encapsulated fertilizers occurs gradually. Such fertilizers reside in soil much longer than conventional soluble mineral fertilizers. The moisture of soil can change during longer period depending on the weather conditions. It is therefore important that the properties of coatings would be as much as possible stable at the changeable conditions of environment.

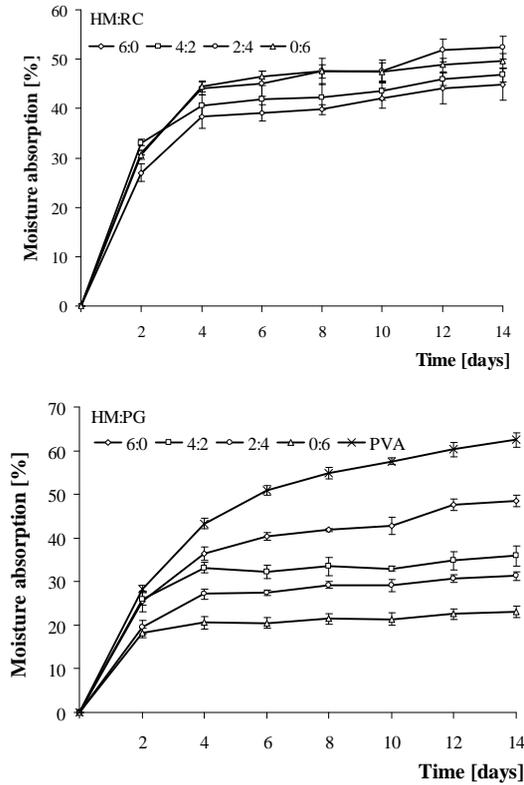


Fig. 4. Moisture absorption of the composite films with different mass ratio of the filler components as a function of storage time at RH of 100%. Mass ratio PVA:filler = 4:6

When the films of the composites were placed into the environment saturated with water vapour the layer of condensate appeared on their surface. It is therefore likely that glycerol and other water soluble components of the composites can migrate into this layer. This can cause the change of the properties of the composite films. We have estimated the changes of the density, dimensions surface area of the films after keeping them for 14 days in the environment saturated with water vapour and then dried in a desiccator with silica gel for 1 week. The results of the measurements are given in Table 4. The density of the films of the composites after exposure of them to 100% relative humidity decreased. The changes of dimensions were found to be lower for those films which contained more phosphogypsum. The dimensions of the composites films containing horn meal and rapeseed cake experienced much larger changes. The surface area of the films decreased by 20%. This decrease was accompanied by the increase of the density of the composites.

We have studied the possibilities of encapsulation of mineral fertilizers by the polymer composites described in this work and estimated the influence of the films used for encapsulation on the rate of release of the fertilizers. The composites of PVA with horn

meal, rapeseed cake and phosphogypsum with the mass ratio of PVA and filler of 4:6 were used for encapsulation.

Table 4
Stability of density and dimensional stability of the films of the composites after exposure to moisture and drying

Mass ratio of the components	Density [g/cm ³]		Change values	Decrease of the surface area [%]
	Initial	After exposure to moisture and drying		
PVA:HM:RC				
4:6:0	0.76±0.02	0.67±0.04	-0.09	17.8
4:4:2	0.78±0.03	0.83±0.03	+0.05	20.8
4:2:4	0.79±0.03	0.87±0.02	+0.08	22.3
4:0:6	0.91±0.02	1.00±0.02	+0.09	21.0
PVA:HM:PG				
4:4:2	0.83±0.03	0.73±0.04	-0.10	17.3
4:2:4	0.96±0.04	0.86±0.03	-0.10	16.4
4:0:6	1.05±0.01	0.99±0.02	-0.06	3.4
PVA:RC:PG				
4:4:2	0.99±0.02	0.97±0.02	-0.02	10.4
4:2:4	1.02±0.02	0.96±0.02	-0.06	4.5
10:0:0	0.94±0.04	1.05±0.03	-0.11	2.9

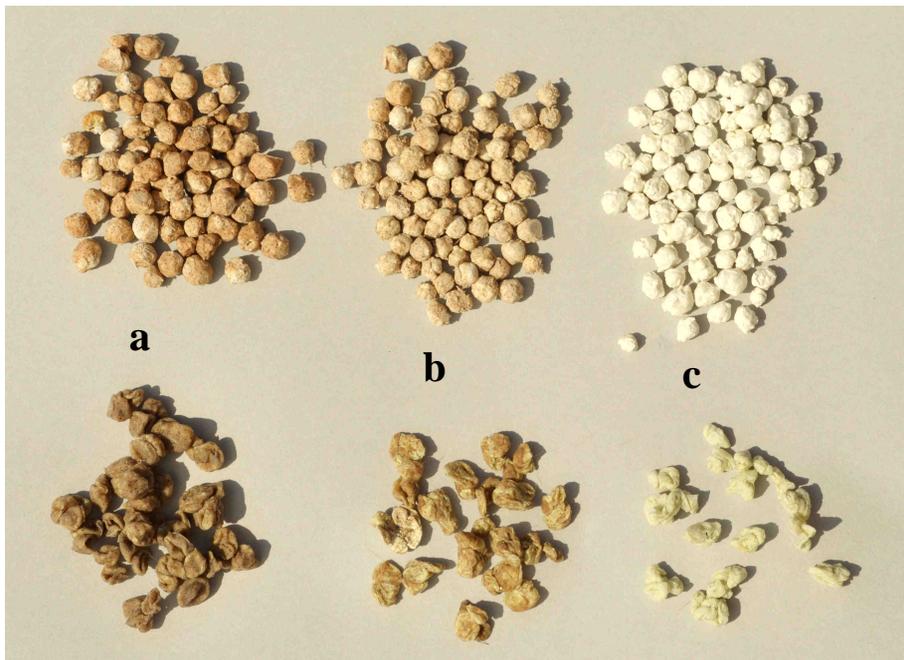


Fig. 5. Particles of fertilizers covered by films of the composites of PVA with rapeseed cake (a), horn meal (b) and phosphogypsum (c) before (above) and after keeping in water for three hours (below)

Encapsulation was performed in the following way. The granules of mineral fertilizers ($1\pm 0.001\text{g}$) with the diameter of 2-3 mm were immersed into the mixture of the composite, took out and after removal of the excess of the encapsulation mixture they were dried at 80°C and then cooled down to the room temperature and weighed. The mass of coatings was found to be different when the composites with the different fillers were used for encapsulation. For the composites containing RC, HM and PG it constituted 6.9, 3.6 and 2.9% respectively from the mass of the fertilizers encapsulated. The encapsulated fertilizers obtained were immersed in distilled water and the effect of the composite coatings on the rate of dissolution of the fertilizers was studied. Figure 5 shows the encapsulated fertilizers before and after keeping them in water for three hours. It was estimated by measuring the conductivity of the solutions which was the measure of the concentration of the dissolved substances. The results presented in Figure 6 show that encapsulation results in the increase of the time of release of the fertilizers.

After 60 min of exposure to water of the fertilizers encapsulated with the composites containing RC, HM and PG as the fillers the comparable conductivities of 5.61, 6.19 and 5.6 mS/cm respectively were observed. For the non-capsulated fertilizers the conductivity of 9.38 mS/cm was recorded. This value is almost limiting. After the exposure of the non-capsulated fertilizers to water for 180 min the electrical conductivity of 10 mS/cm was observed.

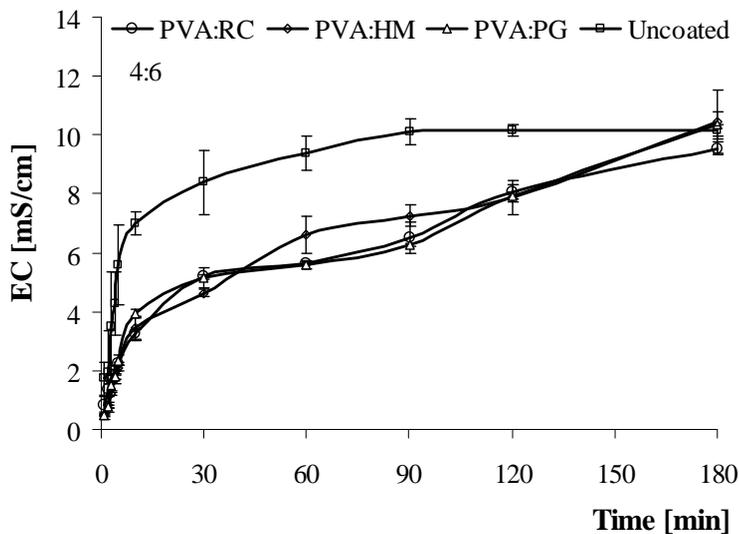


Fig. 6. Electrical conductivity versus time for obtained after immersion into distilled water of the uncoated fertilizers and those coated by films of the composites of PVA with horn meal, rapeseed cake and phosphogypsum. Mass ratio PVA:filler = 4:6

Considering the mass ratios of the coatings and the fertilizers we can state that the composites containing PG and HM are more effective. The same effect is achieved with the smaller amount of the composite on the surface of the fertilizers. This observation correlates with the results of investigation of the properties of the composite films. The addition of PG

increases the density and elasticity of the films and decreases their hygroscopicity. The films of the composites containing HM were found to be less soluble and less hygroscopic than those containing RC. Thus by variation of the components of the composites and of the thickness of the films it is possible to obtain the coatings for the encapsulation of the fertilizers with the desirable permeability. Suherman and Anggoro [12] have studied the influence the films prepared from the mixture of starch, acrylic acid and polyethylene glycol on the rate of dissolution of the urea granules and established the dissolution rate of the granules decreased with increasing concentration of starch and decreasing bed temperature. However it has to be noted that there are almost no reports on the influence of the fillers of the different origin on the properties of the coatings of the granular fertilizers.

Conclusions

Composites with the various concentration of nitrogen and phosphorus were prepared using polyvinyl alcohol as a polymer binder, horn meal, rapeseed cake and phosphogypsum as a filler and crude glycerol as a plasticizer and as a phosphorus containing additive. The influence of the fillers and their mixtures on the properties of the composites was studied. The composite films containing phosphogypsum exhibited higher elasticity the films of the composites containing horn meal or rapeseed cake. The films in which the mass ratios PVA:HM, PVA:RC and PVA:PG were 4:6 exhibited the tensile strength of 10.2, 14.0 and 4.95 MPa respectively. Elongation at break of the same series of films was found to be 5.58, 4.14, 121% respectively while the tensile modulus was 442, 432 and 152 MPa correspondingly. When the mixtures of horn meal and rapeseed cake were used as the fillers, the mass ratio of these components did not have any substantial effect on the mechanical properties of the composites. The addition of phosphogypsum resulted in the increase of elasticity and hardness of the composite films. The films of the composites containing phosphogypsum showed lower hygroscopicity and higher stability of dimensions than those containing horn meal and rapeseed cake or their mixtures as the fillers. The composites developed were used for encapsulation of mineral fertilizers. It was established that encapsulation resulted in the increase of the time of release of the fertilizers. These encapsulated fertilizers represent a combination of inorganic and organic fertilizers. Since assimilation of organic substances is considerably longer, nitrogen and phosphorus of these components is available for plants much later than inorganic nitrogen and phosphorus. Thus the composite film not only decreases the rate of desorption of the mineral components from the granules of the fertilizers but also prolongs the impact of the fertilizers on the plants. The selection of the different fillers enables to obtain the coatings for the granules of fertilizers containing the different amounts of nutrients.

Acknowledgments

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BIODEGRADOWALNE KOMPOZYTY POLIMEROWE WYPEŁNIONE ODPADAMI ZAWIERAJĄCYMI AZOT I FOSFOR

Abstrakt: Wytworzono materiały kompozytowe, składające się z alkoholu poliwinylowego, zawierające odpady z azotem i fosforem. Badano możliwości zastosowania tych materiałów do kapsułkowania nawozów mineralnych. Jako wypełniacze kompozytów były wykorzystywane produkty uboczne wytwarzania biopaliwa do silników wysokoprężnych (makuch rzepakowy, surowy glicerol), mączka rogowa (produkt odpadowy z produkcji pasmanteryjnej) i fosfogips (produkt uboczny produkcji nawozów fosforowych). Wytworzono folie kompozytowe z różnymi ilościami azotu i fosforu, różnymi wypełniaczami lub ich mieszaninami. Badano właściwości mechaniczne folii, ich higroskopijność i rozpuszczalność w wodzie. Otrzymane kompozyty zostały wykorzystane do kapsułkowania nawozów mineralnych. Stwierdzono, że kapsułkowanie spowodowało zwiększenie czasu uwalniania nawozów. Opracowane nawozy powolnego uwalniania stanowią kombinację związków nieorganicznych i organicznych. Organiczna część składa się z mączki rogowej i makucha rzepakowego, zawierających azot i fosfor. Ponieważ asymilacja substancji organicznych jest znacznie dłuższa, azot i fosfor z tych składników będą dostępne dla roślin znacznie później niż z substancji nieorganicznych. W ten sposób folia z kompozytu nie tylko zmniejszy szybkość desorpcji składników z granulek nawozów, ale również przedłuży wpływ nawozów na rośliny.

Słowa kluczowe: kompozyty, makuch rzepakowy, mączka rogowa, nawozy, kapsułkowanie, powolne uwalnianie