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# RESEARCH ON THE EFFECTIVENESS OF ENCAPSULATED UREA GRANULES IN POLYMERS

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***Abstract***

*The encapsulation of fertilisers and pesticides represents an important process in agriculture and plays a significant role in the crop productivity. In literature, there is an explosion of data regarding the production and use of biodegradable polymers and the encapsulation of fertilizers, pesticides or their mixtures is also recorded. The aim is to control the release of the active substance over time, not only to extend the period of time during which it acts but also to prevent the pollution of ground water due to the washing processes. At the same time, it also aims to improve working conditions regarding the transport and use of fertilizers and pesticides.*

***Key words**: biodegradable polymers, encapsulation, urea.*

## INTRODUCTION

The global demand for synthetic fertilizers which can affect crop productivity has increased during the past few years (Trenkel, 2010). The research based on biodegradable polymers used as coatings for slow-release fertilisers is increasing as they provide a more efficient alternative with a less negative environmental impact (Li et al., 2021). Despite the fact that the use of slow release fertilizers is still limited due to increased costs, they were shown to improve agricultural efficiency (Akelah, 1996). The absence of nitrogen in the soil tremendously affects the industry (Leghari et al., 2016). Hence, urea based fertilisers were developed to meet this demand (Azeem et al., 2014). The discharge of nitrogen from urea needs to be controlled in order to avoid losses, such as $NH_3$ volatilization, which can increase the level of pollution as well as the cost of fertilizers (Horrigan et al., 2002). The ability to coat urea with biodegradable materials can also improve the functioning of the soil (Matson et al., 1998).

The process of encapsulation consists of polymer synthesis followed by the addition of those on granules of fertilizers using different methods (Ni et al., 2011). Considering this, two polymers were used: one of them was synthesised by sulphonating $C_2$-$C_3$ rubber in order to encapsulate the granules of urea (spraying technique) and the other one was polyethylene rubber with a low molecular weight, also used for encapsulation.

## MATERIALS AND METHODS

Synthesis of sulphonated $C_2C_3$ rubber, also known as S-EPDM (sulphonated ethylene propylene diene monomer rubber)
EPDM (30 g) and toluene (330 g) were added in a triple neck round bottom flask (1L capacity) with a magnetic stirrer, thermometer and condenser attached. The temperature of the mixture was kept to $60^0$C with the aid of a thermostat. After the rubber was fully dissolved (2 hours), acetic anhydride (11 mL) was added and the solution was stirred for 30 minutes. Sulfuric acid (4 mL, 95%) was added and the

sulphonation occurred after 1 hour. The sulphonated polymer was neutralised with sodium hydroxide (6 g) in a methanol/toluene azeotropic mixture (methanol: toluene = 120: 46.5 g). The solution can be used as it is or dilluted with toluene in order to obtain a fine film of polymer on the urea granules (from 2 to 100 $\mu$m, with the most suitable film having a 2-20 $\mu$m thickness).

Urea granules (25 granules) were used to determine the barrier properties of polymer film used to encapsulate it. Hence, for the first type of polymer, the solution which was obtained after synthesis was sprayed on the granules of urea with a specialised glass sprayer. The process of spraying and drying was repeated three times to ensure that the layer of polymer film has a reasonable consistency. Additionally, the ethylene oligomer was melted and sprayed directly on the urea granules. To determine the barrier properties of the polymer film, the granules of urea were immersed in distilled water (200 $cm^3$, T = $20^0$C). After 24 hours, the granules were separated using gravity filtration and immersed in fresh distilled water (200 $cm^3$).

The amount of urea released in 24 hours was determined using the method presented below, using two samples of aqueous solution of urea: one containing 20 g of this solution and another one containing 40 g. The analysis can be gravimetric, volumetric or colorimetric. An aqueous solution (100 mL) containing urea (40-50 mg) was added to a beaker. Anhydrous acetic acid (30 mL) and Xanhidrol (25 mL, 10% solution in anhydrous ethanol or 1% solution in acetic acid) were added whilst stirring. The solution was added in small portions (5 mL) every 20 and 10 minutes. The product of the reaction is kept for 24 hours and then filtered using a G-3 crucible glass filter with sintered disc. Initially, gravity filtration is performed followed by slow vacuum filtration using a water aspirator. The product obtained was washed with a saturated solution of 1,3-di(9H-xanthen-9-yl) urea in ethanol (20 mL) and dried at 100$^o$C for 1-1.5 hours before being weight.

## RESULTS AND DISCUSSIONS

There are multiple advantages to encapsulating fertilizers, pesticides or the mixtures of those, such as economical advantages but also advantages which involve the current climate crisis. Hence, the process of encapsulating in order to control the release of the chemicals can have a significant influence of the environment:

- the release of the active substance into the soil is performed slowly, under control, which determines a prolonged biological activity of the fertilizers, pesticides or their respective mixtures;
- the pollution of the ground water which is determined by the washing processes caused by heavy rain is avoided;
- when both fertilisers and pesticides are applied at the same time, this causes serious energetical savings and the number of treatments applied needs to be reduced;
- superior work conditions are ensured during the packing, shipping and using periods.

Considering all of the previously mentioned advantages, the process of obtaining fertilisers, pesticides and their mixtures encapsulated in polymer film is not trivial at all. Hence, it is absolutely necessary to run a feasibility study which can help to determine one of the procedures that needs to be used. It is important to notice that for developing countries the cost (price) of the procedure is not as important as the final goal that needs to be achieved.

In order to perform the encapsulation of the fertilisers, pesticides and their mixtures there have been multiple studies. The results obtained by the multiple researching groups were published and they are starting to be applied in various industries.

Historically, microcapsules represent core/shell particles where the shell is manufactured from a semi-impermeable polymer film and the core is made of the active substance: the fertiliser, pesticide or the mixture.

There are multiple ways of encapsulating the previously mentioned active substances, such as:

- polymerization in emulsion, which is obtained by taking into consideration the core/shell principle;
- encapsulation through direct spraying of the molten mass of polymer on the fertiliser granules, called “Hot melt coating”;
- encapsulation by spraying a solution made of polymers in organic solvents;
- encapsulation aqueous solutions of fertilisers;
- encapsulation by forming the polymer “in situ” as a result of poly-condensation or poly-addition processes (Crosslinkable Coating);

- encapsulating fertilizers in the polymer gel;
- encapsulation by forming hydrogen bonds between the fertilizer and the polymer.

As a result of these processes, two different types of fertiliser granules are obtained:

- granules covered on the exterior by a semi-impermeable membrane made of polymers;
- monolithic granules in which the fertiliser is trapped in a polymeric matrix or dry hydrogel.

In this experiment, the granules of fertiliser are being sprayed using a solution of polymer in a solvent or in a solvent-cosolvent mixture, with the process being followed by evaporation of the solvent at a temperature, under a normal pressure or under vacuum, depending on its boiling temperature. Furthermore, the list of solvents is not limited at all. Hence, aromatic hydrocarbons (benzene, toluene, xylene, mesitylene), aliphatic hydrocarbons (hexane, toluene, n-octane, 2-ethyl-hexane, 2-ethylcyclohexane) as well as chlorinated derivatives (dichloromethane, trichloromethane, tetrachloromethane, trichloroethylene, tetrachloroethylene).

The spraying process is achieved in machines which function in fluidised layer. The method of obtaining the fertiliser capsules was described in the literature and allows the achievement of thin and uniform covering film. When it comes to polymers, a variety of polymers can be used and a lot of them are modified through sulphonation. In order to reduce the viscosity of the polymer solutions, it is advisable to introduce a polar cosolvent which is capable of solubilising pendant ionomeric groups. The hydrophilic cosolvent must possess a solubility parameter between 10-11 and its weight proportion in the system to be between 0.01% and 15% related to the total organic mixture.

The hydrophilic cosolvent is decided between the following classes of compounds: alcohols, amides, amines, acetamides etc. We are mentioning that aliphatic alcohols (methanol, ethanol, n-propanol, isopropanol, 1,2-propandiol, the monomethylether of ethylene glycol as well as n-ethylformamide or methyl-isobutyl carbinol) are preferred as polar cosolvents.

Extraordinary results can be obtained if, at the solutions of sulphonated polymer, a basic polymer is added, capable of forming complexes through acid-base interactions. A very interesting method relies on spraying granules of fertiliser in vacuum. According to this method, the granules added in the micro-encapsulation machine are vacuumed and, at the time when the spraying process of polymer solution takes place, it is fully absorbed into the pores which can be found on the surface of the granules. It is worth mentioning that this procedure can be used to spray aqueous dispersions of polymers (e.g. Copolymers of ethene with unsaturated carboxylic acids).

*The mechanism of controlled release of fertilisers*

Despite the chosen method of encapsulation, when the product is inserted into the soil, when it gets in contact with the humidity within it a controlled release takes place of the fertiliser or/and the pesticide. The polymers used for encapsulation can be biodegradable or not. Usually, polymers which contain backbones formed by C-C units tend to be not biodegradable. The insertion of heteroatoms onto the backbone can offer biodegradability. Most of the time, the controlled release of fertiliser occurs in the presence of water. When water passes through the polymer capsule, the hydrophilic polymer can expand which allows the controlled release of the active substance. The release can also be related to the increased osmotic pressure due to the penetration of water in the semi-permeable membrane of the polymer.

Tables 1 and 2 represent a comparison between the results obtained and the literature values. These values were used to obtain two graphs corresponding to the two different polymers analysed: EPDM and polyethylene (He et al., 2000). The analysis of the graphs suggests that the results are reliable, taking into consideration the type and the coating thickness of the polymer film. These influence the release rate of the urea into the soil (Hodosan, 2007). When two molecules of xanhidrol are added to urea (Figure 1) a hydrophobic condensation product is obtained which is used in its quantitative determination. It was found that 0.142 mg of urea correspond to 1 mg of 1,3-di(9H-xanthen-9-yl) urea. For correction, 0.5% of the value obtained is added to the result.

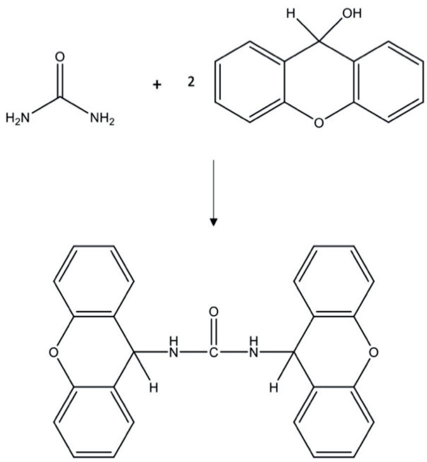


Figure 1. Reaction between urea and xanhidrol to give the desired product

Table 1. Results obtained in order to determine the barrier properties of the S-EPDM polymer film

| No. Days | POLYMER: S-EPDM | | |
|---|---|---|---|
| | g urea/ 20 g sample | g urea cumulated | % urea released |
| 1 | 0.4804 | 0.4804 | 19.216 |
| 2 | 0.2302 | 0.716 | 28.424 |
| 3 | 0.1918 | 0.9024 | 36.096 |
| 4 | 0.2097 | 1.1121 | 44.484 |
| 5 | 0.0959 | 1.2080 | 48.320 |
| 6 | 0.1525 | 1.3605 | 54.420 |
| 7 | 0.0479 | 1.4084 | 56.336 |
| 8 | 0.1519 | 1.5603 | 62.412 |
| 9 | 0.1223 | 1.6826 | 67.304 |
| 10 | 0.1616 | 1.7842 | 71.368 |
| 11 | 0.1243 | 1.9085 | 76.340 |
| 12 | 0.0461 | 1.9546 | 78.184 |

Table 2. Results obtained in order to determine the barrier properties of the polyethylene polymer film

| No. Days | POLYMER: POLYETHYLENE | | |
|---|---|---|---|
| | g urea/ 40 g sample | g urea cumulated | % urea released |
| 1 | 0.1108 | 0.1108 | 2.216 |
| 2 | 0.0642 | 0.1750 | 3.500 |
| 3 | 0.0352 | 0.2102 | 4.204 |
| 4 | 0.0150 | 0.2252 | 4.504 |
| 5 | 0.0369 | 0.2621 | 5.242 |
| 6 | 0.0629 | 0.3250 | 6.500 |
| 7 | 0.1572 | 0.4822 | 9.644 |
| 8 | 0.0478 | 0.5300 | 10.600 |
| 9 | 0.3904 | 0.9204 | 18.408 |
| 10 | 0.3998 | 1.3202 | 26.404 |
| 11 | 0.1901 | 1.5103 | 30.206 |
| 12 | 0.3458 | 1.8560 | 37.122 |
| 13 | 0.3761 | 2.2322 | 44.644 |

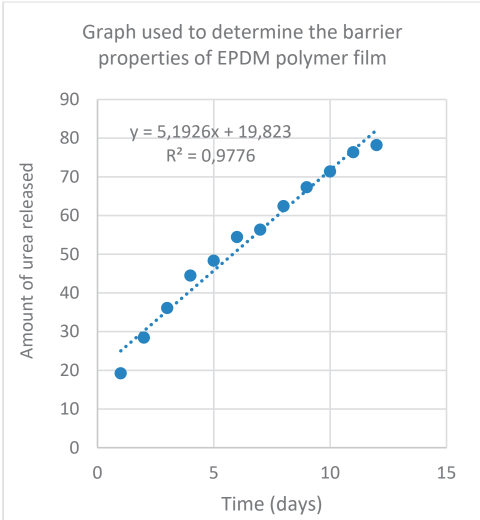


Figure 2. Graph used to determine the barrier properties of EPDM polymer film

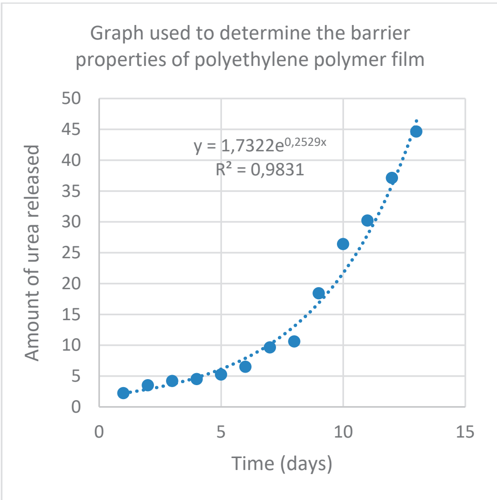


Figure 3. Graph used to determine the barrier properties of polyethylene polymer film

*The direct encapsulation of polymers on the fertiliser granules using the Hot Melt Coating technique*

The encapsulation of fertilisers using this procedure consists of spray coating the molten mass of polymer or mixture of polymers directly on the surface of the fertiliser granules in machines in fluidised layers or in spherical machines which rotate continuously.

When it comes to polymers, generally products with the melting temperature between 30° and 120° are used as well as mixtures of petroleum

wax with polyethylene with the molecular weight <10000, copolymers ethylene-vinyl acetate, copolymers ethylene-carbon dioxide, copolymers of ethene with $\alpha$-olefins, aliphatic polyesters etc.
An interesting example of controlled slow-release consists of attaching the fertiliser to the main backbone through covalent bonds which hydrolyse easily in the presence of water, releasing the fertiliser. A polymer like this one is polyvinylic alcohol in which the hydroxyl groups have normal reactivity and react with the groups already present in the fertiliser.
In the literature, there are examples in which the fertiliser is attached to the polymer backbone through hydrogen bonds. In this case, the polymer must contain functional groups which are able to form these hydrogen bonds. These groups could be: -OH; $-NH_2$; -NH-; $-SO_2NH-$; $-SO_2NH_2$; -CONH; $-CONH_2$; -COOH; -CON<; =N-; -N=N-.
No matter what the nature of the mechanism of controlled release of the fertiliser or its mixture with pesticides is, it is important to ensure that the duration of the mechanism of action is prolonged for longer compared to the treatment with normal fertiliser which is not encapsulated. It is necessary to obtain these mixtures of fertilisers with pesticides and their encapsulation since this is the basis of modern and sustainable agriculture. This is required due to the significant changes in the economy as well as the impact on the environment since a lot of chemicals are toxic and could potentially harm humans over a longer period of time. Additionally, the pollution of the groundwater needs to be avoided.
Taking into consideration the results obtained in this experiment, it is undoubtedly necessary to encapsulate fertilisers and pesticides in order to improve their action but also to protect the environment.

## CONCLUSIONS

The encapsulation of fertilisers and pesticides has been proven to efficiently and effectively improve the crop production as well as diminish the levels of chemicals found in the soil. There are multiple industrial procedures which can achieve the encapsulation and the most common one involves spray coating with a mixture of polymers.
In this experiment, urea was encapsulated using two types of polymers: sulphonated EPDM rubber (with the sulphonation being achieved in the lab using an original method) and polyethene with a low molecular mass. The analysis of the barrier properties of the products suggested that the results obtained are reliable by comparing them to literature values for similar polymers. Furthermore, the sulphonation of EPDM rubber can be achieved with a standard procedure, but the encapsulation of the urea granules is obtained by spraying whilst they were present in the solution (toluene/methanol with rubber) which requires the recovery of the toluene and methanol after the spraying process.
The presence of methanol in the system is vital to the solubilisation of the hydrophilic ionomer. The sodium present in the neutralised sulphonic groups can be replaced by zinc, one of the main microelements which aids the growth of plants. It is very effective to use ethylene oligomers to encapsulate urea due to the fact that the price is low and the spraying process is achieved using specialised machinery for powdering fertilizer granules in order to prevent their crowding. This process is considered to be the only suitable one considering the economical situation in our country.
The results obtained support the evidence that the encapsulation process is necessary and further research should be conducted in order to determine the most accurate and efficient procedure as well as the best polymers chemical compounds which can be used to encapsulate fertilisers.

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