

Use of Polyhydroxybutyrate and Ethyl Cellulose for Coating of Urea Granules

Milene M. E. Costa,[†] Elaine C. M. Cabral-Albuquerque,[†] Tito L. M. Alves,[§] José Carlos Pinto,[§] and Rosana L. Fialho^{*,†}

[†]Laboratório de Polímeros e Bioprocessos - Programa de Pós-Graduação em Engenharia Industrial, Universidade Federal da Bahia, Rua Aristides Novis 2, Federação, Salvador BA 40210-630, Brazil

[§]Laboratório de Engenharia de Polímeros - Programa de Engenharia Química/COPPE, Universidade Federal do Rio de Janeiro, Cidade Universitária, CP: 68502, Rio de Janeiro RJ 21945-970, Brazil

ABSTRACT: Fertilizers contain essential nutrients for agricultural growth and development. However, most nitrogen fertilizers are substances with high solubility of ions and are very susceptible to leaching and volatilization. To minimize these losses, an alternative is the creation of a physical barrier around granules. One way is to coat granules with polymers. In the present work urea granules were coated with polyhydroxybutyrate and ethyl cellulose in various conditions in the presence of emulsifiers. The original granules and the final products were characterized by scanning electron microscopy, Fourier transform infrared spectroscopy and thermogravimetry, to evaluate the surface morphology, the interaction between the granules and the coating, and the rates of mass change. The rates of urea release in distilled water were measured with a commercial enzyme kit. It is shown that those polymers are effective for coating of granules, leading to reduction of rates of urea dissolution in water.

KEYWORDS: urea fertilizer, coating, slow release

■ INTRODUCTION

Urea is by far the most used fertilizer in agriculture. The worldwide production of urea in 2012 was about 184 million metric tons.¹ The popularity of urea is due to important characteristics, such as its high nutrient content (46.6 wt % of nitrogen), low production costs, solubility in water, non-corrosive properties, and easy mixing with other compounds.^{2–4}

A main problem associated with the use of urea as a fertilizer is the high rate of loss to the environment through leaching and volatilization.^{5–10} Environmental losses can represent about half of the total amount of applied urea fertilizer, depending on the climate, soil conditions, and application technologies, thereby causing environmental pollution and increasing the costs of crop production.^{11–14} A possible alternative to reduce nutrient losses is the development of slow-release or controlled-release fertilizers, by coating urea granules with materials that present lower water solubilities.^{6,12–14}

Coating of urea particles can be performed using a physical process (for example, by casting with a polymer solution) or a chemical process (for example, by promoting a surface reaction between urea and formaldehyde). The selection of the coating materials determines the final quality of the controlled-release fertilizer. Coatings should be cheap, present good coating properties, and not contaminate the environment.¹⁵ Particularly, biodegradable polymer materials (polyacid lactic,¹⁶ ethyl cellulose,¹⁷ starch,¹⁸ chitosan¹⁹) have often been used for the coating of urea granules mainly because they can be degraded by microorganisms.²⁰ Furthermore, they allow for improved retention of macro- and micronutrients in the coated particles, reducing dissolution rates in water and consequently environmental losses.²¹ However, the efficiency of the polymer coating depends significantly on the physical and chemical

interactions between the polymer material and the fertilizer and on the homogeneity of the produced polymer shell. This efficiency may be improved by modifying the polymer or by adding additives, such as compatibilizing agents.²²

Surprisingly, the effects of adding compatibilizers to the polymer solutions used to coat urea particles with biodegradable polymer films have not been studied in detail. This is particularly true when solutions of polyhydroxybutyrate (PHB) and ethyl cellulose (EC) are considered. For this reason, the commercial compatibilizers Triton X-100, cetyl trimethylammonium bromide (CTAB), and sodium lauryl sulfate (SLS) are added to PHB and EC solutions to analyze how the compatibilizers affect the characteristics and morphology of polymer films produced during coating of urea granules through distinct processes.

On the basis of the previous remarks, the main objective of the present work is to coat urea granules with PHB, a biodegradable polymer currently used for the production of biomedical implants, drug coating, and packaging devices,²³ or EC, a biodegradable polymer already used for film coating of agricultural products,¹⁷ in the presence of different commercial compatibilizers. To achieve a proper coating, the effects of the commercial compatibilizing agents Triton X-100, CTAB, and SLS (emulsifiers that act at the interfaces of immiscible materials, reducing the interfacial tension) and operation conditions (production process) are analyzed for the first time. The original urea granules and the obtained coated products are then characterized through scanning electron

Received: April 29, 2013

Revised: September 19, 2013

Accepted: September 23, 2013

Published: September 23, 2013

Table 1. Details of Product Preparation

product	polymer	solvent	concn of polymeric solution	CA	% coating
IM-PHB					<0.35
IM-PHB/T X-100				Triton X-100	<0.35
IM-PHB/SLS				SLS	<0.35
IM-PHB/CTAB	PHB	CHCl ₃	5% (w/v)	CTAB	<0.35
IM-PHB/SLS+CTAB				SLS and CTAB	<0.35
PL-PHB					3.82
PL-PHB/CTA				CTAB	4.41
IM-PHB+EC	PHB and EC		2.5% (w/v) PHB and 2.5% (w/v) EC		1.38
IM-PHB//EC	EC	CH ₃ (CO)CH ₃	5% (w/v)		1.37
IM-PHB/SLS//EC					1.09
IM-PHB/CTAB//EC					1.79

microscopy (SEM) to evaluate the surface morphology of the granules, Fourier transform infrared spectroscopy (FTIR) to determine possible interactions between the components of the coating and the urea granules, and thermogravimetry (TGA) to evaluate the rate of mass change as a function of temperature. Kinetic urea release experiments in distilled water are also performed to determine the rate of urea release in aqueous solution. It is shown that the addition of compatibilizers to the casting polymer solutions affects significantly the morphology of the coated urea granules and that the compatibilizer effect depends on the particular analyzed coating process. The best coating results were obtained when CTAB was added to solutions of PHB sprayed onto urea granules, which includes slower rates of urea release in water.

MATERIALS AND METHODS

Materials. Industrial urea (46.4% nitrogen) was provided as granules (average particle size = 1.84 mm) by Petróleo Brasileiro S.A. (Unit Operations Nitrogen Fertilizer Factory in Camaçari, Bahia). PHB (high purity, $M_w = 5 \times 10^5 \text{ g mol}^{-1}$) was purchased from Usina da Pedra (São Paulo, Brazil). EC was purchased from Dow Chemical, with trade name Ethocel (bulk density = 0.4 g/cm³). Chloroform (99.8%, $M_w = 119.38 \text{ g mol}^{-1}$) was purchased from Synth, Brazil. Acetone (99.5%, $M_w = 58.08 \text{ g mol}^{-1}$) was obtained from Nuclear, Brazil. Triton X-100 or polyethylene glycol *p*-(1,1,3,3-tetramethylbutyl)phenyl ether ($M_w = 625.0 \text{ g mol}^{-1}$), CTAB ($M_w = 364.45 \text{ g mol}^{-1}$), and SLS ($M_w = 288.38 \text{ g mol}^{-1}$), used as compatibilizing agents, were obtained, respectively, from Sigma-Aldrich, Vetec Fine Chemical, and Reagen Quimibrás, Brazil. The enzyme urease and other reagents used in the hydrolysis of urea to determine its released amount are part of the kit Uréia 500 from Doles Ltda., Brazil. All reagents and solvents used were of analytical grade and had not undergone any prior purification and were used directly as purchased. The only exception was the urea granules, which were kept at 70 °C for 1 h prior to removal of water.

All experiments were performed in triplicate.

Coating. PHB and EC were used for coating of urea in solutions of chloroform and acetone, which also contained some additives. Two distinct strategies were used for the production of coated particles:

(a) *Immersion.* Urea granules were immersed directly into the chloroform solutions under continuous magnetic stirring, filtered, and left to dry on a glass plate, as discussed below.

(b) *Spraying.* Urea granules were sprayed with a manual pulverizer with trigger (output between 0.6 and 0.9 mL/spray). To hinder the formation of agglomerates, granules were mixed manually and dried as described below.

To produce urea granules coated with PHB, 1.50 g of polymer was solubilized in 30 mL of chloroform. To produce coatings with PHB and EC, 0.75 g of PHB and 0.75 g of EC were solubilized in 30 mL of chloroform. The solutions were maintained under magnetic stirring at 380 rpm at 40 °C for 10 min. When a compatibilizing agent (CA) was used, 1.50 g of CA was added to the polymer solution under the same

conditions. Twenty grams of urea granules was added to the solution, and the mixture was kept in a closed system under magnetic stirring at 100 rpm at 24 °C for 1 h.

To produce urea granules coated with EC through immersion, 0.75 g of EC was solubilized in 30 mL of acetone and maintained under the same aforementioned conditions. Twenty grams of urea granules previously coated with PHB was used as a core for coating with EC.

In the spraying process, 1.50 g of PHB was solubilized in 30 mL of chloroform (380 rpm, 40 °C, and 10 min), and 20.0 g of urea was sprayed with the polymeric solution under continuous manual mixing at 70 °C.

After coating, granules were sieved and placed in a vent chapel for 2 h for the slow evaporation of the solvent. Finally, the coated urea granules were placed in an oven at 70–80 °C for 1 h to ensure the complete removal of the solvent.

The coating efficiency was characterized by placing a known mass of product, M_{total} (g), in 100 mL of distilled water at room temperature (24 °C), ensuring that the mass of urea was below the saturation limit. After complete dissolution of the nutrient, the obtained polymer dispersion was filtered with a quantitative paper filter and washed with distilled water. The filter was dried at 120 °C for approximately 4–6 h, and the residual material was weighed, M_{polym} (g). The coating efficiency was calculated as

$$\% \text{ polym} = \frac{M_{\text{polym}} \text{ (g)}}{M_{\text{total}} \text{ (g)}} \quad (\text{eq 1})$$

where % polym is the percentage of polymer added to the urea granules, M_{polym} (g) is the mass of residual polymer, and M_{total} (g) is the total mass (urea + polymer) of the analyzed product.

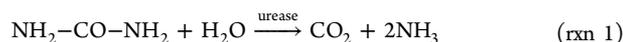
Table 1 describes the products prepared.

Characterization. Analyses were performed with a scanning electron microscope, model Quanta 200, manufactured by Fei Company (Hillsboro, OR, USA), operating at 20 kV. Previously, the products had been metalized with gold in a sputtering device, model JFC-1500, manufactured by JEOL (Peabody, MA, USA), with current in the range between 4 and 5 mA. The thickness of the deposited gold was approximately 300 Å.¹⁶

Fourier Transform Infrared Spectroscopy. The products were analyzed using two different IR instruments. A direct analysis of products was performed at room temperature in a mid-IR spectrophotometer, model Nicolet 6700, manufactured by Thermo-Electron Corp. (Waltham, MA, USA). In addition, analysis of the KBr pellets was performed at room temperature in an FTIR spectrophotometer, model Spectrum 100 FTIR, manufactured by Perkin-Elmer (Shelton, CT, USA). Prior to the analyses, the KBr and product samples were ground (about 400 mg of KBr and between 2 and 4 mg of sample). The homogeneous powder mixture was used for the preparation of tablets (about 13 mm in diameter), which were inserted into the analyzer.^{16,29}

Thermogravimetry. Analyses were performed with a calorimeter, model STA 6000, manufactured by Perkin-Elmer. Analyses were performed with a heating rate of 10 °C/min under a continuous flow of nitrogen at a pressure of 40 psi.^{16,29}

Release Profile of Urea in Distilled Water. In vitro tests were prepared by placing known masses (0.25 g) of product in 100 mL of distilled water at 24 °C. The system was homogenized with slight manual agitation before the withdrawal of portions (1 mL) for analysis. Samples were withdrawn at defined time intervals (0, 0.5, 1, 2, 3, 5, 10, 30, and 60 min). The system volume was kept constant by adding distilled water immediately after sampling. The samples were diluted (1 mL of aliquot for 4 mL of water) to maintain the absorbance values in the calibrated range of the spectrophotometer. After dilution, the samples were prepared for analyse using the reagents from kit Uréia 500, manufactured by Doles (Goiânia, Brazil). The kit enables the indirect enzymatic determination of the urea concentration, according to the following reaction:



The urea concentrations were determined by using a calibration model built for a UV-visible spectrophotometer, model Lambda 35, manufactured by PerkinElmer, operating in the wavelength range of 570–720 nm.²⁴

RESULTS AND DISCUSSION

Scanning Electron Microscopy. Figure 1 shows the characteristic surface morphologies of the urea granule and of the final products. The surface morphology of urea (Figure 1a) presents a uniform and wrinkled appearance.

Different coated products were prepared through immersion in PHB solution. IM-PHB (urea granules immersed into 5% w/v PHB solution) (Figure 1b) presents a surface morphology with an appearance that is similar to the surface morphology of urea granules, suggesting that the granules were not coated efficiently; IM-PHB/T X-100 (urea granules immersed into 5% w/v PHB and 5% w/v Triton X-100 solution), IM-PHB/SLS (urea granules immersed into 5% w/v PHB and 5% w/v SLS solution), IM-PHB/CTAB (urea granules immersed into 5% w/v PHB and 5% w/v CTAB solution), and IM-PHB/SLS + CTAB (urea granules immersed into 5% w/v PHB, 2.5% w/v SLS, and 2.5% w/v CTAB solution) (Figure 1c–f) showed different surface morphologies, which suggests the presence of PHB. These products were characterized by the irregular coating, especially the one prepared with CA Triton X-100. The use of CTAB, alone or in combination with SLS, resulted in the most regular and uniform coating morphology.

The products prepared through spraying with PHB solution (PL-PHB, urea granules sprayed with 5% w/v PHB solution; and PL-PHB/CTAB, urea granules sprayed with 5% w/v PHB and 5% w/v CTAB solution) can be observed in Figure 1g,h. These photomicrographs show that both products do not have the characteristic wrinkled aspect observed with urea granules, suggesting the presence of PHB. The particle surfaces are also compact, indicating that coatings produced by spraying result in a regular morphology, especially in the presence of CTAB.

The product IM-PHB+EC (urea granules immersed into 2.5% w/v PHB and 2.5% w/v EC solution) showed a porous surface morphology, as shown in Figure 1i, possibly because of a nonhomogeneous coating formation between PHB and EC, as these materials are not compatible.²⁵

The results were similar even when granules had been coated previously with PHB, using CA or not, and coated with EC afterward (IM-PHB//EC, urea granules immersed previously into 5% w/v PHB solution and then immersed into 5% w/v EC solution; IM-PHB/SLS//EC, urea granules immersed previously into 5% w/v PHB and 5% w/v SLS solution and then immersed into 5% w/v EC solution; and IM-PHB/CTAB//EC, urea granules immersed previously into 5% w/v PHB and 5%

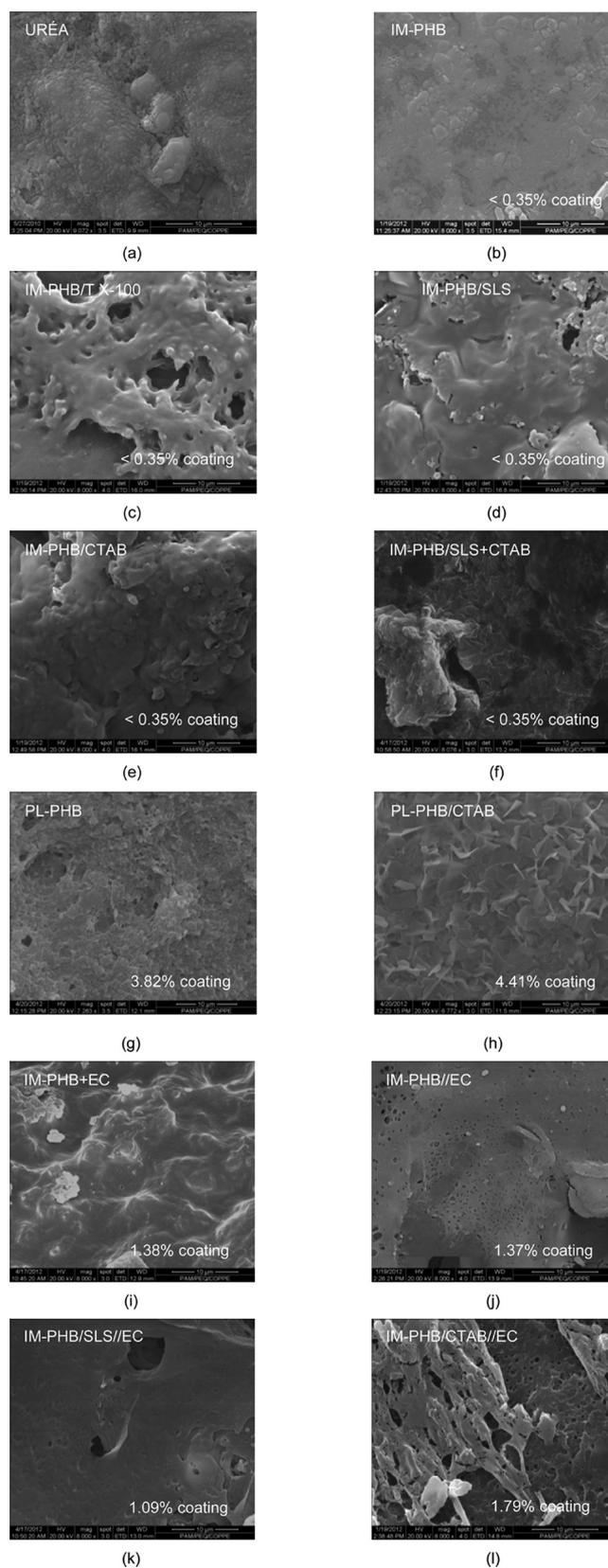


Figure 1. Scanning electron photomicrographs at 10 μm of (a) urea (magnif 9072 \times); (b) IM-PHB, urea granules immersed into 5% w/v PHB solution (magnif 8000 \times); (c) IM-PHB/T X-100, urea granules immersed into 5% w/v PHB and 5% w/v Triton X-100 solution (magnif 8000 \times); (d) IM-PHB/SLS, urea granules immersed into 5% w/v PHB and 5% w/v SLS solution (magnif 8000 \times); (e) IM-PHB/CTAB, urea granules immersed into 5% w/v PHB and 5% w/v CTAB

Figure 1. continued

solution (magnif 8000×); (f) IM-PHB/SLS+CTAB, urea granules immersed into 5% w/v PHB, 2.5% w/v SLS, and 2.5% w/v CTAB solution (magnif 8076×); (g) PL-PHB, urea granules sprayed with 5% w/v PHB solution (magnif 7263×); (h) PL-PHB/CTAB, urea granules sprayed with 5% w/v PHB and 5% w/v CTAB solution (magnif 6772×); (i) IM-PHB+EC, urea granules immersed into 5% w/v PHB and 5% w/v EC solution (magnif 8000×); (j) IM-PHB//EC, urea granules immersed previously into 5% w/v PHB solution and then into 5% w/v EC solution (magnif 8000×); (k) IM-PHB/SLS//EC, urea granules immersed previously into 5% w/v PHB and 5% w/v SLS solution and then into 5% w/v EC solution (magnif 8000×); and (l) IM-PHB/CTAB//EC, urea granules immersed previously into 5% w/v PHB and 5% w/v CTAB solution and then into 5% w/v EC solution (magnif 8000×).

w/v CTAB solution and then immersed into 5% w/v EC solution), as presented in Figure 1j–l. The porous nature of the EC coats was observed also in the production of controlled-release herbicides.^{17,26}

Fourier Transform Infrared Spectroscopy. The products IM-PHB, IM-PHB/T X-100, IM-PHB/SLS, IM-PHB/CTAB, IM-PHB+EC, IM-PHB/SLS//EC, and IM-PHB/CTAB//EC were analyzed by the direct method, whereas the products IM-PHB/SLS+CTAB, PL-PHB, and PL-PHB/CTAB were analyzed by the KBr pellet method.

Figure 2 shows the FTIR spectrum of urea. The products prepared by immersion in a PHB solution presented all of the characteristic bands of urea. IM-PHB/T X-100, IM-PHB/SLS, and IM-PHB/CTAB presented some bands that were not observed in pure urea of C–H stretching (between 3000 and 2840 cm^{-1}) and of C–O stretching (between 1300 and 1000 cm^{-1}), suggesting the presence of surfactant and/or PHB around of the fertilizer. However, just IM-PHB/CTAB showed considerable variations in the characteristic bands of N–H bonds, indicating interactions between the fertilizer and surfactant (Figure 3a).

The interaction between the coating and the urea granules was evaluated with respect to the procedure for coating preparation. The products prepared by spraying with PHB solution also exhibited displacements of the bands related to N–H bonds (Figure 3b,c), but with more intense displacements than those observed in materials prepared by immersion.

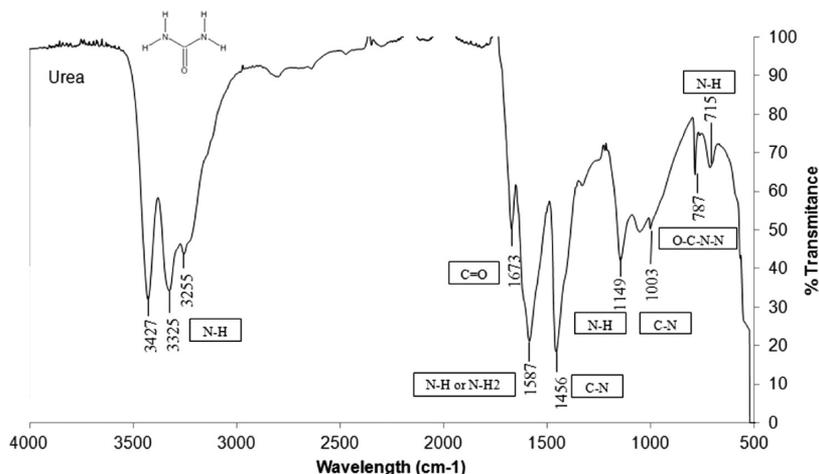


Figure 2. FTIR spectrum of urea.

These observations indicate that the process has some influence on the physical interaction between urea and PHB, represented by the greater amount of coating adhered to the granules (3.82 and 4.41%, respectively).

The infrared data of products prepared with CTAB as CA confirmed the morphological results observed previously, indicating that the more effective interaction promoted by this surfactant leads to formation of more regular coatings, without failures. The supplementary research material presents the infrared bands observed in the range between 3000 and 2840 cm^{-1} , related to the CH₂ and CH₃ bonds of CTAB,²⁷ confirming its interaction with the urea granules.

The product prepared by immersion of urea granules in a polymeric solution of PHB and EC and the products prepared by soaking granules of urea previously coated with PHB in EC solution showed all of the characteristic bands of urea. However, only IM-PHB/CTAB//EC showed significant variations of the characteristics bands of N–H bonds and indicated the presence of characteristic bands of C–H stretching and C–O stretching bonds (Figure 3d). These results indicate that these bands are provided from the interaction between fertilizer and surfactant, confirming that PHB and EC are not compatible.^{25,28}

The spectral analyses allow us to infer that the use of CTAB as CA in the PHB solution provides an efficient interaction between the granule fertilizer and the coating and that the process used for production of the coating can be manipulated to increase the amount of polymer that can adhere to the surface of the granule.

Thermogravimetry. Figure 4 shows the thermal decomposition of urea, where two main stages of mass loss can be observed, one at 66.5% and another one at 32.8%.

This decomposition can be divided into regions of reaction known by different chemical processes associated with the stages of mass loss. Significant loss in the first stage can be observed at approximately 140 °C, associated with the beginning of urea vaporization and the beginning of its decomposition, producing biuret, NH(CO)₂(NH₂)₂. Up to approximately 250 °C, urea continues to decompose; at higher temperatures, biuret starts to decompose and more complex products start to be produced from these decompositions and from self-condensation of biuret.²⁵ The region defined as the second stage, with temperatures above 250 °C, is illustrated by

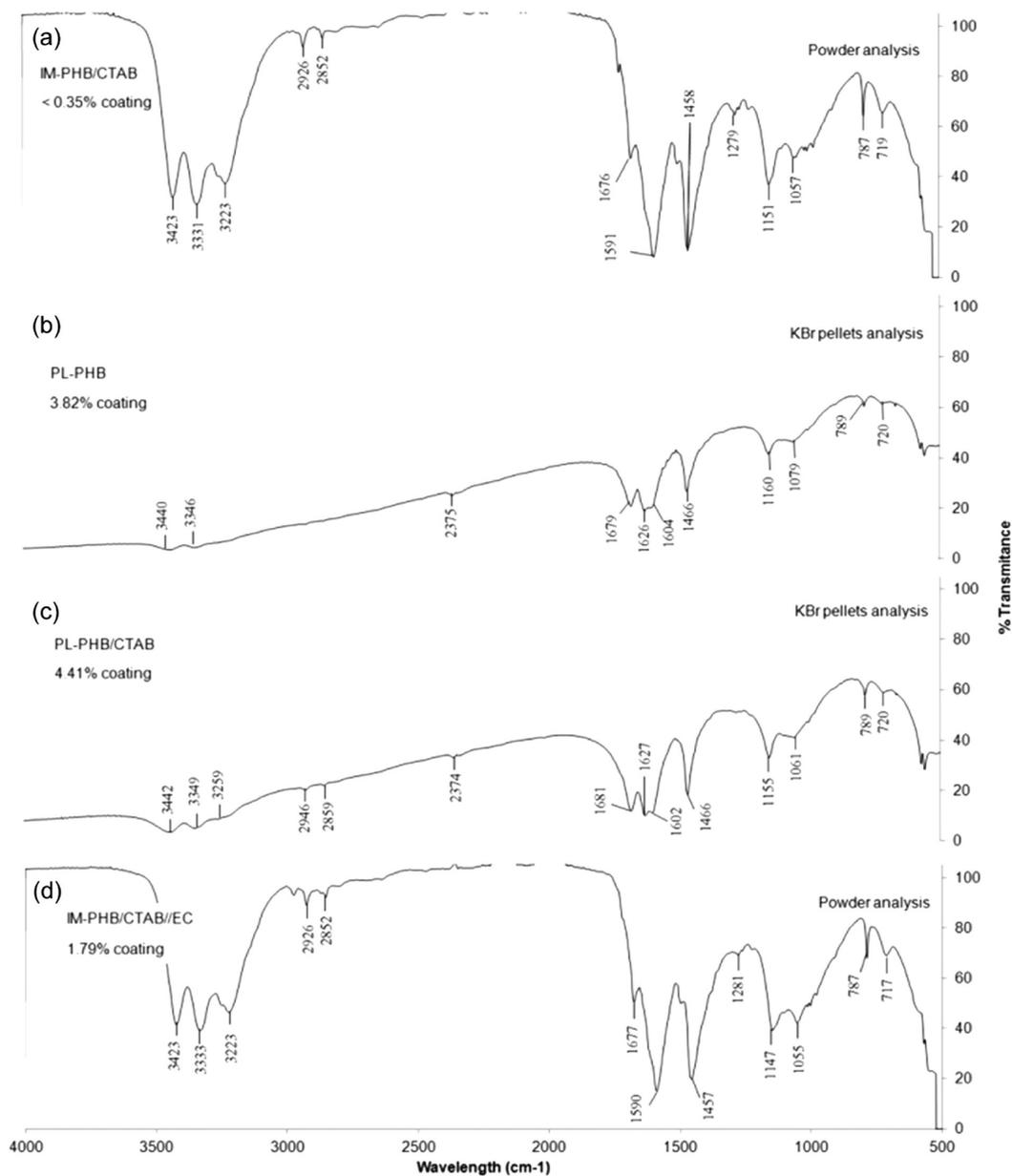


Figure 3. FTIR spectrum of (a) IM-PHB/CTAB (urea granules immersed into 5% w/v PHB and 5% w/v CTAB solution), (b) PL-PHB (urea granules sprayed with 5% w/v PHB solution), (c) PL-PHB/CTAB (urea granules sprayed with 5% w/v PHB and 5% w/v CTAB solution), and (d) IM-PHB/CTAB/EC (urea granules immersed previously into 5% w/v PHB and 5% w/v CTAB solution and then into 5% w/v EC solution).

another stage of significant decrease of mass in the TGA of urea, which can be associated with loss caused by the continuous sublimation and decomposition of the remaining products until complete chemical vaporization and degradation.

The first stage of thermal decomposition of urea is the most important for the purposes of the present study, as this region is related to urea volatilization. Consequently, detailed analysis of the second stage will not be pursued here. All products analyzed showed the characteristic first stage of degradation, always very similar to the first degradation stage of the uncoated urea granules. It can be concluded that the manufacturing process and the coating polymer material influenced the amount of polymer deposited on the granules, but did not affect the original consistency of the fertilizer (core). Similar effects were observed in other products described in the literature and assigned to the low amounts of coating incorporated onto the granules.²⁷ It can be

concluded that the amount of polymer aggregated onto the granule surfaces is too small to modify the characteristic rates of decomposition of urea.

Release Profile of Urea in Distilled Water. Figure 5 shows the release behavior of urea fertilizer and some of the products in distilled water at 24 °C. At the analyzed conditions, >50 wt % of the urea was released within 30 s, whereas complete dissolution was observed after 2 min of analysis. It can also be observed that only products prepared with CTAB in the PHB solution, either alone or in combination with SLS, led to slower rates of urea release, when compared to the other products. However, complete release of urea was observed for these products between 3 and 5 min, with inefficient release rates for applications in the agricultural industry. The fast dissolution of the active agent can be related to the low amounts of polymer adhered onto the granules and to the large

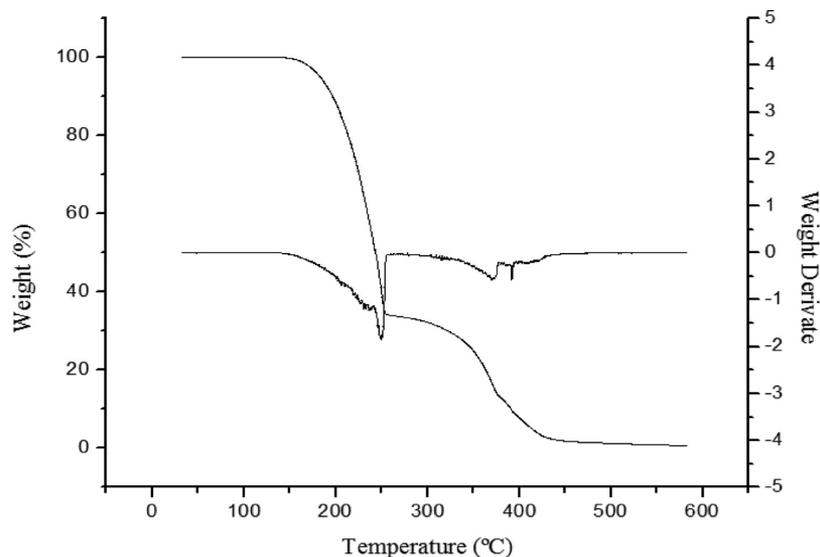


Figure 4. TGA thermogram of urea.

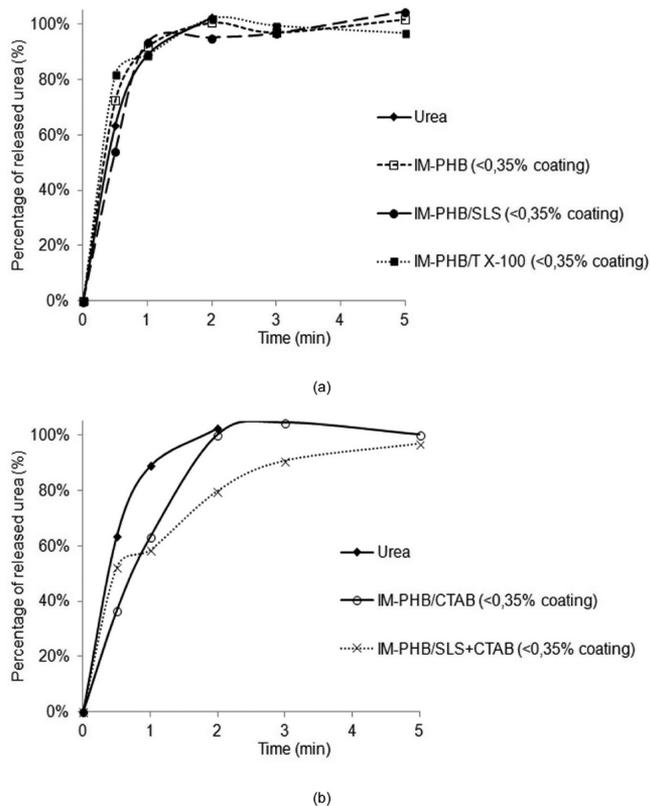


Figure 5. Comparative release profiles of (a) urea, IM-PHB (urea granules immersed into 5% w/v PHB solution), IM-PHB/SLS (urea granules immersed into 5% w/v PHB and 5% w/v SLS solution) and IM-PHB/T X-100 (urea granules immersed into 5% w/v PHB and 5% w/v Triton X-100 solution) ($n = 3$) and (b) urea, IM-PHB/CTAB (urea granules immersed into 5% w/v PHB and 5% w/v CTAB solution), and IM-PHB/SLS+CTAB (urea granules immersed into 5% w/v PHB, 2.5% w/v SLS and 2.5% w/v CTAB solution) ($n = 3$).

number of pores and failures observed on the surfaces, depending on the manufacturing process used.

On the basis of the observations, it can be concluded that CTAB concentration is a possible candidate variable for optimization of the production process and final product

properties. To evaluate the influence of the process used to produce the coating on the final product characteristics, products prepared by spraying PHB solution, with or without CTAB, were analyzed. Rates of urea release of final products can be seen in Figure 6. The release behavior showed again the

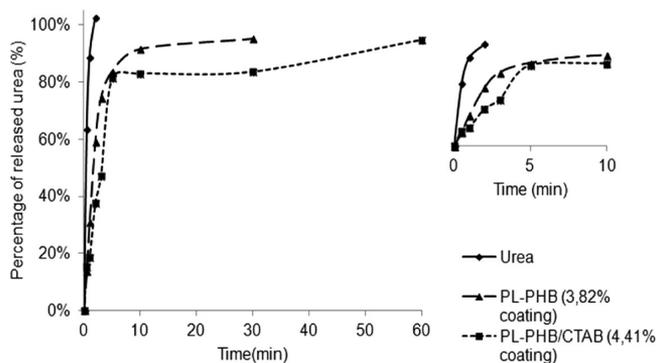


Figure 6. Comparative release profiles of urea, PL-PHB (urea granules sprayed with 5% w/v PHB solution), and PL-PHB/CTAB (urea granules sprayed with 5% w/v PHB and CTAB solution) ($n = 3$).

efficiency of CTAB as a ligand for urea/PHB. The results showed that the spraying procedure was effective in producing a good polymer coating. In this case, half of the urea in the product PL-PHB/CTAB was released in approximately 3 min, whereas 90% of the available urea was dissolved after 1 h in water. These much slower rates of urea release can be associated with the enhanced interaction provided by CTAB and the best utilization and dispersion of the polymer over the granule surface due to the selected production process, which resulted in a much larger percentage of polymer adhered to the granules and a more compact coating.

As CTAB contains nitrogen in its molecule, enzymatic tests were carried out with a solution of 5% w/v of CTAB in water to determine if the CTAB nitrogen could cause interferences during the determination of rates of urea release. As observed experimentally, CTAB tests led to the identification of 0.0005 g of urea, which can be regarded as a very low value. Therefore, CTAB interference on urea release tests can be neglected.

In Figure 7, it can be observed that the product obtained after immersion of urea granules in PHB and EC solution (IM-

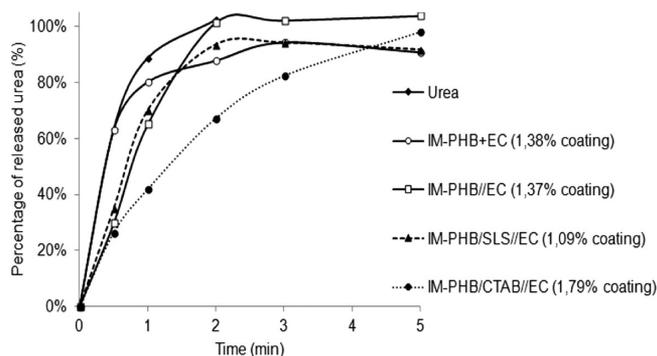


Figure 7. Comparative release profiles of urea, IM-PHB+EC (urea granules immersed into 5% w/v PHB and 5% w/v EC solution), IM-PHB//EC (urea granules immersed previously into 5% w/v PHB solution and then into 5% w/v EC solution), IM-PHB/SLS//EC (urea granules immersed previously into 5% w/v PHB and 5% w/v SLS solution and then into 5% w/v EC solution), and IM-PHB/CTAB//EC (urea granules immersed previously into 5% w/v PHB and 5% w/v CTAB solution and then into 5% w/v EC solution) ($n = 3$).

PHB+EC) showed initial urea dissolution rates that were similar to the ones of uncoated urea, with >50 wt % of urea released in 30 s. This can be associated with irregular surfaces, resulting from the lack of interaction between the fertilizer and the polymer materials. On the other hand, the product obtained after immersion of the previously coated granules with PHB and CTAB in the EC solution presented lower rates of urea release than the uncoated granules due to enhanced interaction provided by the surfactant. Even with the larger amounts of coating incorporated on the granules, products quickly released the active agent, which may be linked to the process used for coating. In these cases, nutrient release was completed after 5 min.

Previous studies have proposed the coating of urea granules by pumping EC solution into a fluidized bed.¹⁵ Although this procedure can provide better distribution of the polymer material on the surface of the granules, it can potentially lead to slower rates of urea release. According to the available information, complete release of urea was obtained after 35–50 h for coated products, which can be compared to about 3 h for uncoated urea (10–15 times slower for coated materials). Release rates were very different because release tests were not performed in pure water and because as much as 10–20 wt % of coating was used.¹⁵ In the present case, release rates were almost 60 times slower for urea granules coated with PHB and CTAB, using much lower amounts of polymer, indicating that the analyzed products and processes can find use in real agricultural applications.

With regard to the comparison between in vitro release tests, as those made in this work, with releasing tests in soil, studies showed that the release rates presented similar profiles, although slower in soil.¹¹ Thus, it can be assumed that the release profiles of the materials produced in this work should provide representative information for soil release tests.

The results indicated that the interaction between the fertilizer granules and PHB was only enhanced with the addition of CA to the polymer solution, producing more uniform films on particles of in natural urea. The CTAB was

the compatibilizing agent that presented the highest incorporation efficiency of PHB on urea, providing slower release rates.

According to the results, we can conclude that the process used in the production of coatings influenced the morphology and the release profiles of the active agent, because the production process is one factor that suggests how the polymer will be organized around the granules. The spraying proved to be the most effective method for the production of coating urea granules. This may be associated with greater use of the polymer, as well as the split atomization of the polymer solution with simultaneous drying, which allows the formation of a coating more uniform and without formation of agglomerates. The results of PL-PHB/CTAB characterization implied that the use of a fluidized bed in fertilizer coating will present better results once coating properties such as film thickness, temperature, and surface profile can be controlled.^{30–32} Furthermore, it will offer the possibility of expanding the scale of production.

Thereby, the coating of urea granules with films of PHB and using CTAB as CA through the spraying method were shown to be promising to reduce nitrogen losses.

AUTHOR INFORMATION

Corresponding Author

*(R.L.F.) Phone: 55 71 3283-9804. E-mail: rosanafialho@ufba.br.

Funding

We are grateful to the Fundo de Amparo à Pesquisa do Estado da Bahia (FAPESB) for financial support.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We are grateful to Petróleo Brasileiro S.A. (Unit Operations Nitrogen Fertilizer Factory of Camacari, Bahia) for the urea granules.

REFERENCES

- (1) Ceresana. Market Study: Urea, 2012; available at <http://www.ceresana.com/en/market-studies/agriculture/urea/> (accessed July 8, 2013).
- (2) Hettiarachchi, G.; Premarayhna, L.; McLaughlin, M.; Kirby, J.; Stacey, S.; Chittleborough, D. Selenate-enriched urea granules are a highly effective fertilizer for selenium biofortification of paddy rice grain. *J. Agric. Food Chem.* **2012**, *60*, 6037–6044.
- (3) Gowariker, V.; Krishnamurthy, V. N.; Gowariker, S.; Dhanorkar, M.; Paranjape, K. *The Fertilizer Encyclopedia*; Wiley: Hoboken, NJ, USA, 1999.
- (4) IFA: Production and trade statistics. International Fertilizer Industry Association, 2010; available at <http://www.fertilizer.org/ifa/HomePage/STATISTICS/Production-and-trade> (accessed Jan 16, 2012).
- (5) Newbould, P. The use of nitrogen fertilizer in agriculture. Where do we go practically and ecologically? *Plant Soil* **1989**, *115*, 297–311.
- (6) Shaviv, A. Advances in controlled release of fertilizers. *Adv. Agron.* **2000**, *71*, 1–49.
- (7) Pereira, E. I.; Minussi, F. B.; da Cruz, C. C. T.; Bernardi, A. C. C.; Ribeiro, C. Urea-montmorillonite extruded nanocomposites: a novel slow-release material. *J. Agric. Food Chem.* **2012**, *60*, 5267–5272.
- (8) Yang, Y. C.; Zhang, M.; Li, Y. C.; Fan, X. H.; Geng, Y. Q. Improving the quality of polymer-coated urea with recycled plastic, proper additives, and large tablets. *J. Agric. Food Chem.* **2012**, *60*, 11229–11237.

- (9) Milani, N.; McLaughlin, M. J.; Stacey, S. P.; Kirby, J. K.; Hettiarachchi, G. M.; Beak, D. G.; Cornelis, G. Dissolution kinetics of macronutrient fertilizers coated with manufactured zinc oxide nanoparticles. *J. Agric. Food Chem.* **2012**, *60*, 3991–3998.
- (10) Ni, B. L.; Liu, M. Z.; Lu, S. Y.; Xie, L. H.; Wang, Y. F. Environmentally friendly slow-release nitrogen fertilizer. *J. Agric. Food Chem.* **2011**, *59*, 10169–10175.
- (11) Dave, A. M.; Soppimath, K. S. A review on controlled release of nitrogen fertilizers through polymeric membrane devices. *Polym.—Plast. Technol.* **1999**, *38*, 675–711.
- (12) Guo, M.; Liu, M.; Liang, R.; Niu, A. Granular urea-formaldehyde slow-release fertilizer with superabsorbent and moisture preservation. *J. Appl. Polym. Sci.* **2006**, *99*, 3230–3235.
- (13) Tao, S.; Liu, J.; Jin, K.; Qiu, X.; Zhang, Y.; Ren, X.; Hu, S. Preparation and characterizations of triple polymer-coated controlled-release urea with water-retention property and enhanced durability. *J. Appl. Polym. Sci.* **2011**, *120*, 2103–2111.
- (14) Suherman, I.; Anggoro, D. D. Producing slow release urea by coating with starch/acrylic acid in fluid bed spraying. *Int. J. Eng. Technol.* **2011**, *11*, 77–80.
- (15) Ko, B.-S.; Cho, Y.-S.; Rhu, H.-K. Controlled release of urea from rosin-coated fertilizer particles. *Ind. Eng. Chem. Res.* **1996**, *35*, 250–257.
- (16) Hanafi, M. M.; Eltaib, S. M.; Ahmad, M. B. Physical and chemical characteristics of controlled release compound fertilizer. *Eur. Polym. J.* **2000**, *36*, 2081–2088.
- (17) Fernandez-Perez, M.; Garrido-Herrera, F. J.; Gonzalez-Pradas, E.; Villafranca-Sánchez, M.; Flores-Céspedes, F. Lignin and ethylcellulose as polymers in controlled release formulations of urea. *J. Appl. Polym. Sci.* **2008**, *108*, 3796–3803.
- (18) Guo, M.; Liu, M.; Zhang, F.; Wu, L. Preparations and properties of a slow-release membrane-encapsulated urea fertilizer with superabsorbent and moisture preservation. *Ind. Eng. Chem. Res.* **2005**, *44*, 4206–4211.
- (19) Wu, L.; Liu, M. Preparation and properties of chitosan-coated NPK compound fertilizer with controlled-release and water retention. *Carbohydr. Polym.* **2008**, *72*, 240–247.
- (20) Ray, S. S.; Bousmina, M. Biodegradable polymers and their layered silicate nanocomposites: in greening the 21st century materials world. *Prog. Mater. Sci.* **2005**, *50*, 962–1079.
- (21) Trenkel, M. E. Controlled release and stabilized fertilizer in agriculture – improving fertilizer use efficiency. *Int. Fert. Ind. Assoc.* **1997**, 156.
- (22) Avella, M.; Martuscelli, E.; Raimo, M. Review properties of blends and composites based on poly(3-hydroxy)butyrate (PHB) and poly(3-hydroxybutyrate-hydroxyvalerate) (PHBV) copolymers. *J. Mater. Sci.* **2000**, *35*, 523–545.
- (23) Chen, C.; Zhou, X.; Zhuang, Y.; Dong, L. Thermal behavior and intermolecular interactions in blends of poly(3-hydroxybutyrate) and maleated poly(3-hydroxybutyrate) with chitosan. *J. Polym. Sci., Part B: Polym. Phys.* **2005**, *43*, 35–47.
- (24) Doles Reagentes e Equipamentos para Laboratório Ltda., Uréia 500, 2011.
- (25) Scandola, M. Polymer blends based on bacterial poly(3-hydroxybutyrate). *Can. J. Microbiol.* **1995**, *41*, 310–315.
- (26) Fernandez-Perez, M.; Villafranca-Sánchez, M.; Flores-Céspedes, F.; Daza-Fernández, I. Ethylcellulose and lignin as bearer polymers in controlled release formulations of chloridazon. *Carbohydr. Polym.* **2011**, *83*, 672–1679.
- (27) Supplementary Material, The Royal Society of Chemistry. *J. Mater. Chem.* 2001.
- (28) Schaber, P. M.; Colson, J.; Higgins, S.; Thielen, D.; Anspach, B.; Brauer, J. Thermal decomposition (pyrolysis) of urea in an open reaction vessel. *Thermochim. Acta* **2004**, *424*, 131–141.
- (29) Junejo, N.; Khanif, M. Y.; Hanafi, M. M.; Wan, Z. W. Y.; Dharejo, K. A.; Abdu, A. Evaluation of coated urea for the effects of coating on the physical and chemical properties of urea fertilizer. *Int. J. Phys. Sci.* **2012**, *7*, 1932–1937.
- (30) Donida, M.; Rocha, S. Coating of urea with an aqueous polymeric suspension in a two-dimensional spouted bed. *Dry. Technol.* **2002**, *20*, 685–704.
- (31) Tzika, M.; Alexandridou, S.; Kiparissides, C. Evaluation of the morphological and release characteristics of coated fertilizer. *Powder Technol.* **2003**, *132*, 16–24.
- (32) Lan, R.; Yonghui, L.; Wang, G.; Wang, T.; Kan, C.; Jin, Y. Experimental modeling of polymer latex spray coating for producing controlled-release urea. *Particuology* **2011**, *9*, 510–516.