Controlled release of nitrogen-source fertilizers by natural-oil-based poly(urethane) coatings: The kinetic aspects of urea release

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ABSTRACT: Urea is the most common source of nitrogen fertilizer, but it has serious disadvantages with respect to volatilization and leaching; these can be controlled by polymeric coatings on the granules. However, the effectiveness of this strategy depends on the formed polymer presenting good adhesion, reactivity with the urea surface, uniformity, and efficient release kinetics control. Therefore, in this study, we evaluated the release kinetics of urea coated by polyurethane produced from two oils (soybean and castor) by analyzing the influence of the thickness, coating stability, deposition interface, and total release time. The results demonstrate that castor oil produced superior materials, which achieved a total release time in water immersion of over 40 days with a total coating mass of less than 4% of the total mass. The good interface suggested that this material may produce coatings of good quality and long release times with minimum thickness, and this will maximize the total nitrogen present in the granule. © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43790.

INTRODUCTION

World population growth has as direct relation to the increasing search for highly productive and sustainable agriculture, so there is a proportionality to the use of fertilizers.[1] Thus, it is important to develop control technologies for these substances in the environment. For example, there is urea, which meets the diverse requirements of nitrogen replacement fertilization, although high losses occur that are mainly linked to leaching and volatilization.[2–4]

As a result, a solution that has been proposed to control and reduce the amount of fertilizer applied to the soil and/or plants, with a major impact on cost reduction and the side effects of drift and/or excess application, is the use of coatings on fertilizers (or granules).[5,6] The function of this coating is to protect and prevent the fast release of the fertilizer into the environment through the formation of a membrane, usually semipermeable, and with permeability control.[7,8] It should also have a hardness that effectively protects the substrate (fertilizer), with good resistances to mechanical abrasion and moisture permeation.[9]

In the specialized literature, some studies have been reported that propose various materials to coat nutrients.[10] However, in general, the recommendations indicate thick coatings, which reduce the total amount of nutrient present in the granule. For example, in a study by Li *et al.*,[11] urea granules were coated with acrylic polymer; this resulted in a final material with a 32.5% total N (urea = 45.1% total N). Furthermore, the hydrophilic character of this polymer resulted in the coating solubilizing over time; this reduced the amount of the barrier that was effective to the diffusion of urea into the medium. In general, despite the importance of this aspect, many reports have not mentioned the total amount of nitrogen present in the granules, with this aspect neglected. Thus, it is desirable for the polymer to be a hydrophobic coating with good interaction with urea and a high mechanical strength to generate a film with controlled diffusion. Polyurethane (PU), a condensation polymer that can be obtained from plant sources such as oil, has such characteristics, but it needs to be further investigated. In addition, the process of urethane polycondensation is chemically derived from the reaction of an isocyanate [toluene diisocyantes and methylene diphenyl diisocyantes (MDIs)] with a hydroxyl group (modified oils or triglycerides can be used as polyols to produce a partial glyceride, which may be used in the formulation of PUs).[12,13] Figure 1 shows the formation of urethane bonds in polymers.

Additional Supporting Information may be found in the online version of this article.
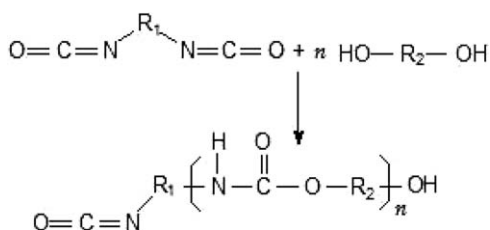
Figure 1. Reaction between diisocyanate and polyol to form PU.

Particularly, one little studied aspect is the nutrient release kinetics, which can help researchers understand the mechanism by which the coating actually controls the nutrient release. In fact, because this release should follow the plant needs (which depend on the target plant, soil, and environmental conditions, among other factors), a deep knowledge of release kinetics is necessary. To the best of our knowledge, diffusion models have not adequately applied this to explain the effect of such coatings on the fertilizer's release processes.

Thus, in this study, we examined the kinetic aspects involved in urea release controlled by a coating with natural-oil-based PUs. To achieve this goal, we synthesized two PU coatings from soybean and castor oil, evaluated their properties, and characterized the kinetic profile of the urea release into aqueous medium. The results presented here suggest that the kinetical profiles could be described by a modified Peppas model,[14] with three main parameters that interpret the diffusion aspects of such coatings. PU was shown to be a material with a good compatibility with urea; it effectively controlled the release over very long periods of time (∼40–75 days) and was effective even at small thicknesses.

EXPERIMENTAL

Preparation of the Materials

We obtained urea granules coated with two PU resin systems that were based on modified vegetable oils (castor and soybean oils). Both were prepared with a commercial MDI (4,4′-diphenylmethane diisocyanate; Desmodur, Bayer) mixed with the respective polyol (castor or soybean oil) at a ratio of 60:40 (mass oil/mass MDI). The coating amounts were calculated from the mass of urea. In a typical procedure, 2.5% coatings (25 g of resin/kg of urea) were prepared by the dispersion of the freshly prepared resin on urea granules (Ureia Fertilizante, Petrobras), typically 3 mm in diameter. With this procedure, 2–10% coatings were prepared for both of the studied systems. The coating process was carried out in a metal turntable rotating at 30 rpm with 20 cm side shields and a 1-kg sample capacity with an air flow between 130 and 140 °C. The resins were standardized with an indirect test of viscosity by fluidity with a Ford viscosity cup (Ford cup viscometer, Gehaka) and flow times of 40–60 s. The quality of the coatings was first measured by deposition on glass slides, and we chose the most visually homogeneous conditions.

The procedure involved only one step for each polymer percentage, and the applied polymer was added with the aid of a pharmaceutical needleless syringe. After homogenization, samples of each percentage were withdrawn, and we repeated the procedure

for the previous covering (2.5, 4.5, and 7.5% for the soybean oil-based resin and 2.5, 4, 5, 7, 8.5, and 9.5% for the castor oil resin). The obtained materials are shown in Figure S1 (Supporting Information).

It should be clarified that in the polymeric structures used, it was possible to establish structures modified with crosslinking agents, with castor oil itself being a kind of triol that favors reticulation. In the case of soybean oil, a modification was made to introduce hydroxyl sites. We made this change starting from the epoxidation with peracetic acid (acetic acid mixed with perhidrol) under a controlled atmosphere at 120 °C with a nitrogen flow. Next, the formation of OH sites active for urethane reactions was made through the addition of methanol in a stoichiometric excess with recovery of the solvent by distillation. To stabilize the modified soybean oil, a stabilizer ($BaSO_4$; Sigma-Aldrich) was physically mixed in the final step (3 wt %). Under the conditions used, an average content of 5.5–6.0% of oxidized groups in the soybean oil was achieved; this resulted in a final material with a hydroxyl number that was near that of castor oil.

After the morphological characterization of the coatings, the experimental and theoretical percentages of materials were evaluated to verify whether the percentages showed a significant variation. To this end, approximately 0.5 g of each material was triturated in triplicate; this solubilized all the urea in distilled water. The urea solubilization was conducted with the aid of an agitator with ultrasound for 20 min; this was followed by filtration to obtain the coating. Finally, the polymers were oven-dried at 30 °C for 48 h and weighed to obtain the polymer mass, as shown in Table I.

Continuing to still evaluated the granules, we determined the total amount of N present because materials intended for agricultural application should possess the greatest possible amount of N, which is the nutrient of interest. This is because when the urea is coated, for a given mass, there is an increase in the amount of polymer; this reduces the urea. However, the polymers used as coating have nitrogen in their structure, so for the determination of the total N of the polymer plus urea, elemental analysis was used. The results of total N from the elemental analysis are shown in Table II.

Table I. Experimental and Calculated Percentages of the Coatings

Material	Calculated value (%)	Experimental average value (%)
Soybean	2.5	2.5 ± 0.1
Soybean	4.5	4.6 ± 0.1
Soybean	7.5	7.5 ± 0.3
Castor	2.5	2.6 ± 0.2
Castor	4.0	4.0 ± 0.2
Castor	5.0	5.0 ± 0.1
Castor	7.0	6.9 ± 0.2
Castor	8.5	8.5 ± 0.2
Castor	9.5	9.6 ± 0.4

Table II. Analysis of the Coated Granules for Determining the Total N Percentage

Material	Total N (%)
Urea	43.21
Soybean 2.5%	41.82
Soybean 4.5%	40.20
Soybean 7.5%	39.59
Castor 2.5%	42.22
Castor 4.0%	41.96
Castor 5.0%	40.85
Castor 7.0%	40.73
Castor 8.5%	40.62
Castor 9.5%	39.46

Physical and Chemical Characteristics of the Coatings

Thermogravimetry (TG) and Differential Scanning Calorimetry (DSC). The thermal analysis technique was used to characterize the polymers and their precursor materials. TG analyses were performed from 30 to 800 °C with heating rate of 10 °C/min in a nitrogen atmosphere with a Q500 TG analyzer instrument (TA Instruments). For DSC analysis, the samples (5–10 mg) were loaded in alumina pans and cycled twice through a temperature range of −80 to 100 °C at a heating rate of 10 °C/min in an N_2 atmosphere (TA Instruments Q2000 instrument).

NMR. NMR spectra were acquired with a a Bruker Avance III HD 9.4 T (400-MHz) spectrometer. Solid-state ^{13}C spectra were obtained by the cross-polarization technique with magic angle sample spinning and high-power decoupling (cross-polarization magic angle spinning). The acquisition parameters were a 40-ms acquisition time, a 4.5-µs contact time, 4096 data points, a 5-s recycle time, and 2048 scans. The samples were packed into 4-mm zirconia-type rotors and spun at 10 kHz. All of the spectra were filtered by an exponential decay function. Hexamethylbenzene (HMB) was used as a chemical shift reference standard (with a methyl line at 17.3 ppm).

X-ray Diffraction (XRD). The XRD studies were performed with a Shimadzu diffractometer (LabX XDR-6000) at 30 kV and 30 mA. Scans were performed in the range between 5 and 70° (with a scan step of 0.02°) with a Cu Kα radiation source with a wavelength equal to 1.54 Å.

Elemental Analysis (CHN). Elemental analyses were performed for pristine and coated granules (urea plus polymer) to determine the total nitrogen value present in the materials because materials with a focus toward application in agriculture must have N quantities greater than 38% when coated. For this determination, we used the 2400 Series II CHNS/O analyzer (PerkinElmer).

Fourier Transform Infrared (FTIR) Spectroscopy. To obtain qualitative results of the groups present in the precursor materials for the formation of PU and to verify the polymer formation, we analyzed the sample materials in the form of KBr pellets in a Nicolet FTIR spectrophotometer in the frequency range from 4000 to 750 cm^{-1} with a 4 cm^{-1} resolution.

Scanning Electron Microscopy (SEM). To characterize the morphology of the urea and polymer coatings, SEM analyses were conducted in a JEOL JSM 6510 equipped with an energy-dispersive X-ray analysis system. This coupled system consisted of an energy-dispersive X-ray spectrometer (Thermo Scientific NSS). The samples were dispersed on carbon tape bonded to the surface of a metal disc (stub) coated with gold in an ionization chamber (BALTEC Med. 020) and analyzed.

Water-Release Assay. The release assays were conducted in 250-mL beakers. Immersed in each beaker was a smaller beaker containing 0.500 g of the coated granules under study; the system was kept under constant stirring at room temperature, as described in the methodology of Bortoletto-Santos and Ribeiro,[15] Pereira et al.,[16] and Giroto et al.[17] The agitation had to be mild to ensure that the urea content measured in the liquid medium was homogeneous and corresponded to the diffusion of the analyzed compound into the medium and its release due to the mechanical action of the stirrer.

The containers were sealed with plastic wrap to minimize evaporative losses, and 500-µL aliquots were taken at different times. The determination of the urea concentration released was analyzed by ultraviolet–visible spectroscopy (Shimadzu 1601 PC) with the method of With et al.[18] The methodology consisted of the preparation of Ehrlich's reagent (5.0 g of dimethylbenzaldehyde plus 20 mL of hydrochloric acid and the completion of the volume to 100 mL with Sigma-Aldrich reagent) and a 10% solution of trichloroacetic acid (Sigma-Aldrich). The sample (500 µL) was mixed with 2.5 mL of the 10% trichloroacetic acid solution and 500 µL of Ehrlich reagent, and absorbance was obtained in the 400–500 nm range.

For comparison, tests with pure material (uncoated) were also performed as a control experiment. The tests and their measurements were simultaneous and done under the same laboratory conditions to ensure a certain equilibrium.

RESULTS AND DISCUSSION

Figure 2 shows the chemical structure of both vegetable oils. The pure soybean oil had no hydroxyl groups in its chain, so a
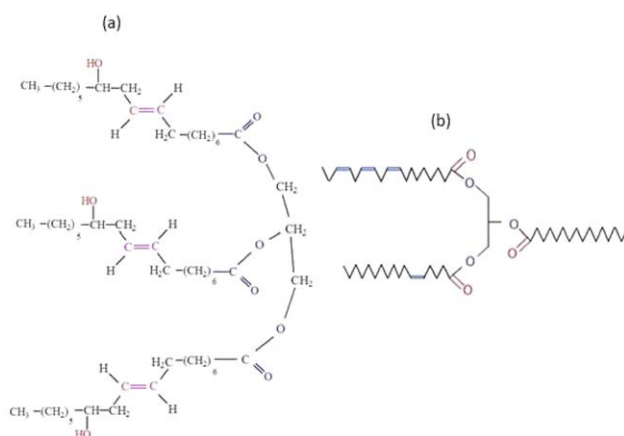
Figure 2. Chemical structures of (a) castor oil (triol glycerol ester of ricinoleic acid) and (b) soybean oil. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
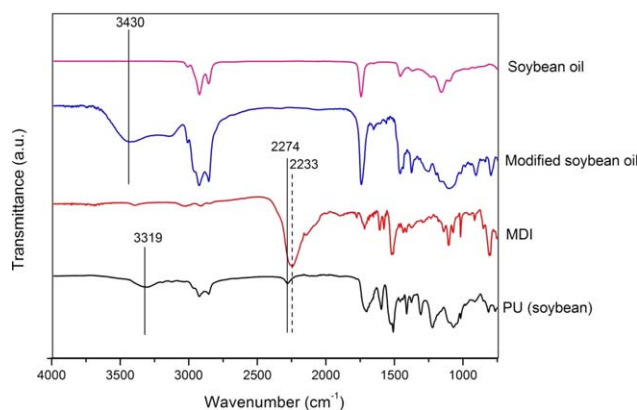
Figure 3. FTIR spectra of the soybean oil after modification and PU soybean formation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

chemical modification was required to introduce these groups, as described in the Experimental section, with epoxidation with peracetic acid followed by methylation. Such a change was not necessary for castor oil because of the presence of OH sites, as shown in the FTIR spectra in Figures 3 and 4. Table S1 (Supporting Information) and the IR spectra (Figure 3) show that there was a modification made to the soybean oil to introduce hydroxyl groups into its structure, as evidenced by the appearance of a broad band at 3400 cm^{-1}, which was characteristic of hydrogen-bond stretching.

Two regions in the spectra also stood out, as shown in Figures 3 and 4; these were connected with the formation of the urethane bonds. The first region was in the 2250 cm^{-1} range and was characteristic of MDI and its NCO groups. The second region was related to the broad band associated with the OH bond. These bands were closely linked to the polymer formation reactive sites. The absence of both bands was noted in the polymer; that is, the NCO groups (derived from the MDI) reacted with OHs groups of the oil. This suggested the formation of the urethane bond, which is represented in the graph by the N—H bond at 3319 cm^{-1}, characteristic of amine N—H stretching.
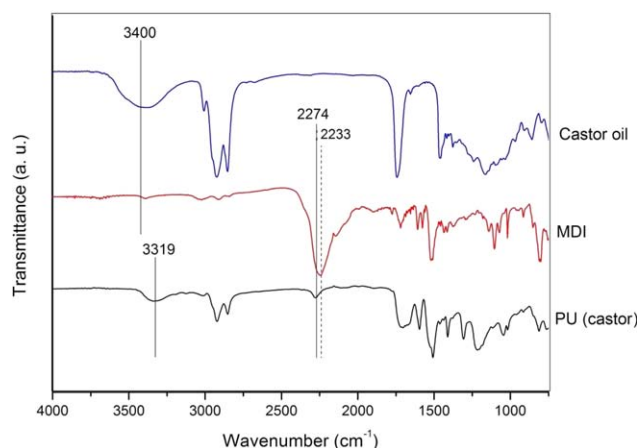

Figure 4. FTIR spectra of the castor oil and PU castor formation. [Color figure can be viewed in the online issue, which is available at wileyonline-library.com.]
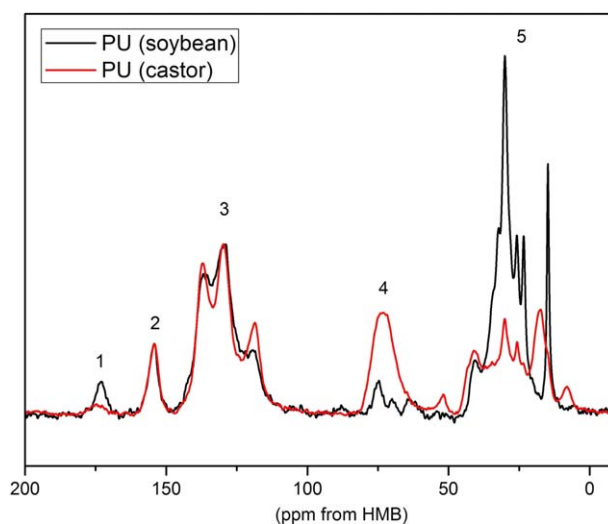

Figure 5. High-resolution solid-state ^{13}C-NMR spectra of the castor and soybean oil PUs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The castor and soybean oil PU formations were also confirmed with high-resolution solid-state ^{13}C-NMR spectroscopy (Figure 5). First, we observed that the spectra of the PUs produced from the two oils were similar. The spectra showed five peaks (or group of peaks), which were assigned to: (1) carboxyl groups at 173 ppm, (2) aromatic C bonded to N (originated from MDI) at 155 ppm, (3) other aromatic C derived from MDI from 140 to 110 ppm, (4) C of the fatty acids esterified with MDI at 75 ppm, and (5) CH$_2$ and CH$_3$ groups of fatty acids C from 37 to 15 ppm.[19,20]

Peak 2 (aromatic C bonded to N) derived from MDI was used to normalize the spectral amplitude. This result shows that the other MDI aromatic peaks were also similar. However, the strong peak 4 in the castor oil sample indicated a higher PU conversion than that in soybean oil. In the same sense, stronger peaks 1 and 5 in the soybean oil sample indicated its low PU conversion. Therefore, this agreed with the TG analysis and also showed residual oil.

Figure 6 shows the XRD peaks of the castor oil PU and soybean oil PU. Because BaSO$_4$ was added as a stabilizing agent to the soybean oil PU, this was also analyzed. The results indicate that both PUs were amorphous polymers with similar reflections at 2θs of 20.22° (for castor oil PU) and 20.24° (for soybean oil PU). A broad peak was observed around 20°; this was characteristic of the standard MDI used in polymer synthesis[21] and showed that the material presented a semicrystalline structure. According to Ali et al.,[22] this was related to the existence of short-range regularly ordered structure of both the hard and soft domains along with the disordered structure of the amorphous phase of the PU matrix, as shown in the values of the reflection plane with interchain spacings of 4.392 and 4.388 Å for castor oil PU and soybean oil PU, respectively. The coating sample showed a low crystallinity profile (only BaSO$_4$ peaks were seen in soybean oil PU).[23]

To determine the degradation behavior of the coating, the materials were subjected to TG analysis, as shown in Figures 7 and
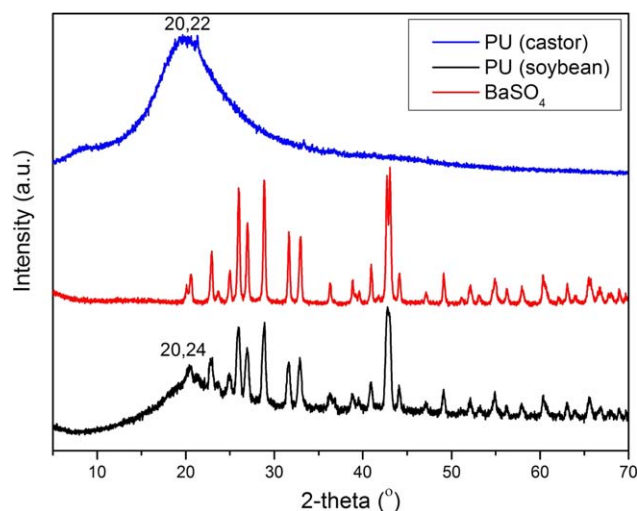
Figure 6. XRD of the PU castor, PU soybean, and BaSO₄. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary. com.]

Figure 8. TG curve and its derivative (DTG) for the soybean oil and soybean oil PU. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

8. Both oils had three mass loss processes, with the first process being responsible for the highest mass loss of about 50%. This first loss was associated with the oxidation of the hydroxyl groups present in the oil structure, and the thermal stability of this process was dependent on the type of oil used.

Also, the castor oil hydroxyl had a higher thermal stability (by the oxidation process) than the soybean oil oxidation because the castor oil had a molecular structure coiled with the inner-facing OH groups to protect them and shift the oxidation temperature range to higher values. This did not occur for the soybean oil: its hydroxyl sites remained exposed toward the outside of the structure.

As shown in Figure 7, the castor oil PU film had three main mass loss processes, with the first between 250 and 300 °C, which was related to PU degradation into isocyanate and alcohol, as observed from the mass loss curve. Next, at 454 °C, there was the formation of primary amine, CO_2, and olefin, and this

process was also responsible for about 40% of the mass loss. Finally, there was the formation of a secondary amine and CO_2; this represented the final process loss.

The same processes were attributed to the polymer derived from soybean oil, although such processes occurred within lower temperature ranges. This lower thermal stability compared to that of castor oil PU was related to an inherited soy structure trait that kept its hydroxyls outside the chain, facilitated the oxidation process, and hence, shifted the oxidation to temperatures lower than those seen in the castor oil PU.

As shown by derivative thermogravimetry (DTG), the presence of a process at 192 °C for the soybean oil PU (Figure 8) was probably due to residual oil lost. Soybean oil had a set of saturated fatty acids that did not undergo modification in their structure and did not participate in the polycondensation reaction; thus, they remained in the polymer structure as an unreacted fatty acid.

The results obtained from DSC analysis (Figures 9 and 10) show a characteristic peak at −28 °C for castor oil, which was present (at −18.8 °C) for the related PU. The same behavior was observed in the soybean oil sample (melting temperature = −5.4 °C) and related PU (−4 °C); in both cases, it showed a possible residual oil (nonpolymerized) on the PU samples. However, because of the interchain attraction in the castor oil molecules, the melting point was very weak compared to that of the soybean oil.[24,25] At the same time, this reflected on the polymerization degree because the residual melting peak in the castor oil PU was very low compared to that of the soybean oil PU. These findings were in accordance with the NMR experiments, which indicated a higher polymerization degree in the castor oil PU sample. Both PU samples showed a crystallization peak at 66 °C, and neither presented a typical glass-transition temperature; this indicated that crosslinking in the oils was possibly very high. In fact, the expected higher interchain attraction in castor oil PU led to a more amorphous material, as shown in the XRD patterns (Figure 6).
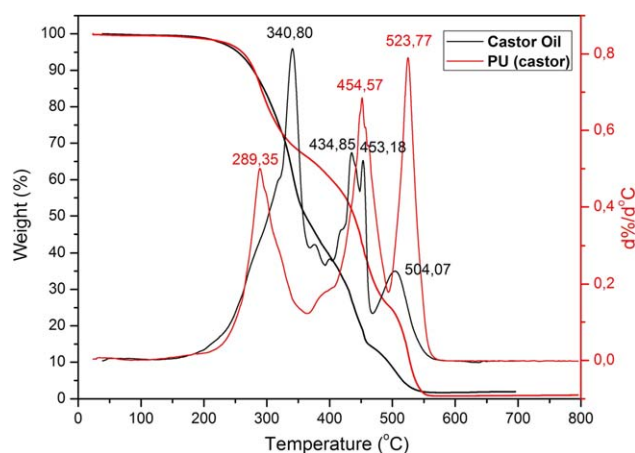

Figure 7. TG curve and its derivative (DTG) for the castor oil and PU (castor). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
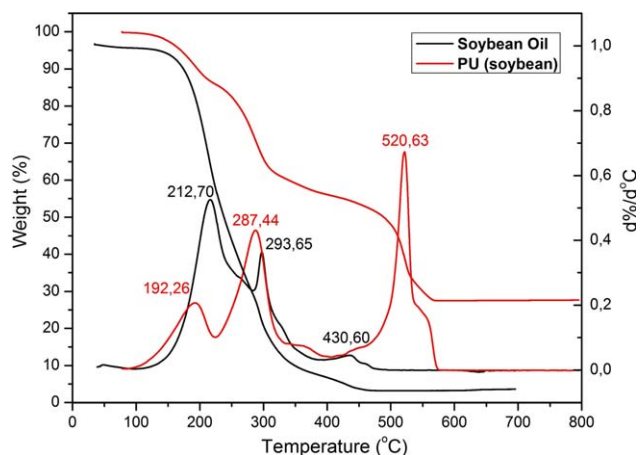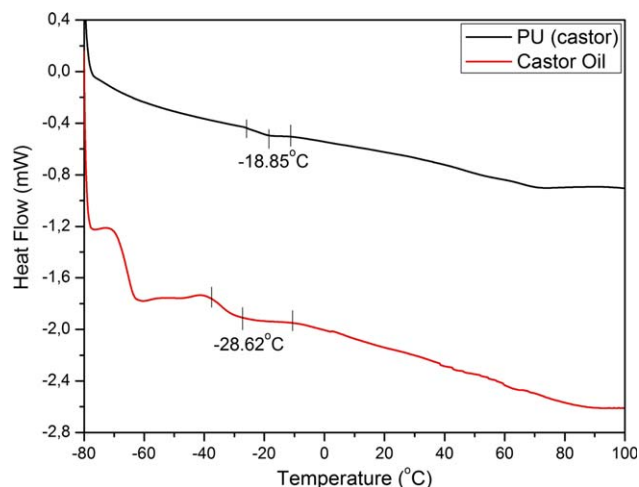
Figure 9. DSC curves for the PU (castor) and castor oil. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary. com.]

Figure 11. SEM of the section containing the interface between the urea and soybean oil PU. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

To understand the profile of the coating between the urea and PU, SEM images were taken. To this end, the coated granules were immersed in liquid N_2; an axial rupture was then promoted to allow us to obtain a section containing urea and polymer. The SEM images for both materials (soybean and castor oil PU) are shown in Figures 11 and 12.

As shown in Figure 11, the formation of a cohesive film with a thickness of approximately 50 µm was observed; the fracture indicated the interfacial region between the film and the urea granules. In this case, we did not consider that this fracture was present in the coated material but that it originated from the sample preparation process. It occurred because of the shrinkage of the material when we inserted the coated granules in liquid nitrogen. As this shrinkage presented distinct behaviors for urea and the polymer, there was breakage of the adhesive line of the coating. However, compared with the results in Figure 12, where
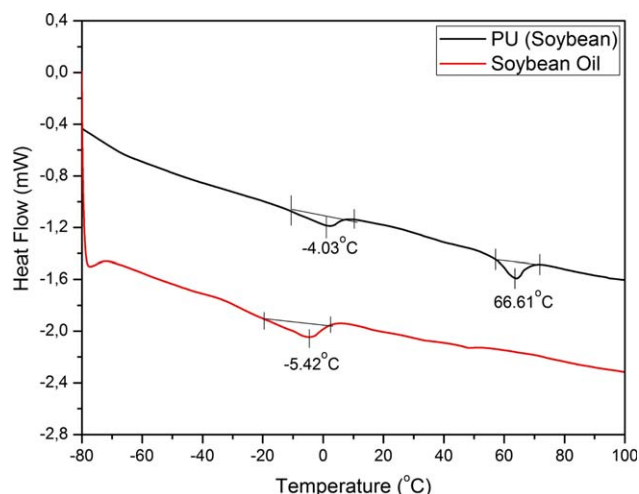
the castor oil coating is shown, the best interfacial quality was observed. This reflects the improved interaction and, therefore, the best accommodation between the urea and castor oil PU, which allowed us to obtain coatings with better adherence.

Figure 13 shows the release of urea into water for different coating percentages. The results show that the variation of the coating level was directly correlated to the release profile. Also, for all materials, the amount of urea released was over 80% of the total coated, and their behavior only stabilized after 200 h in all cases; this characterized the controlled release behavior.

Comparing the results, we observed that the release profile for coatings containing 5% extended beyond 40 days and the castor-oil-based material (4%) had the same release characteristic when compared to the materials with a 7.5% coating (soybean oil PU). This showed that the castor oil PU based coatings were better able to retain/release macronutrients.

Figure 10. DSC curves for the PU (soybean) and soybean oil. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
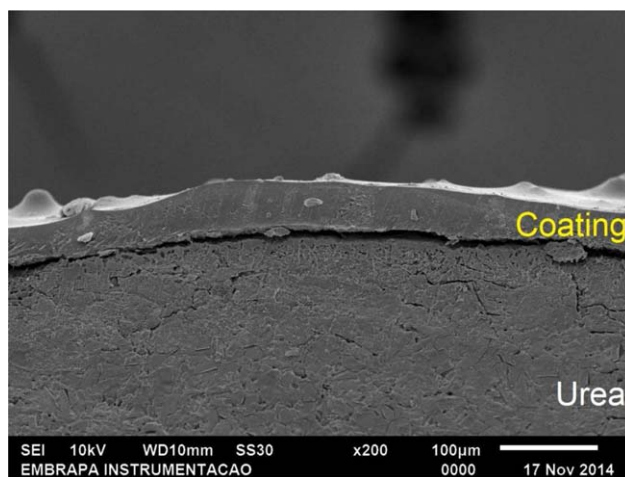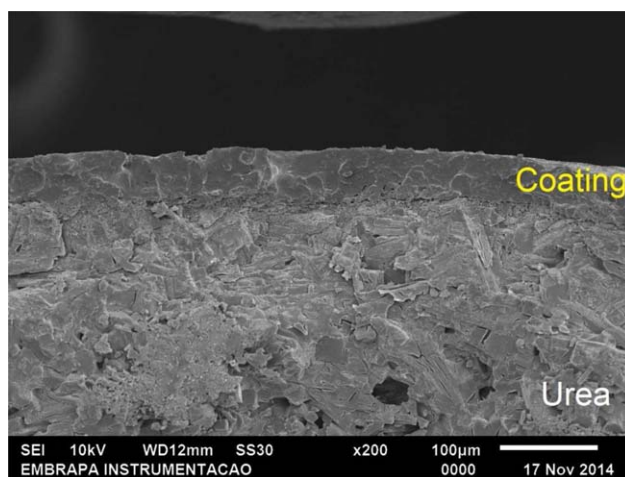

Figure 12. SEM of the section containing the interface between the urea and PU castor. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
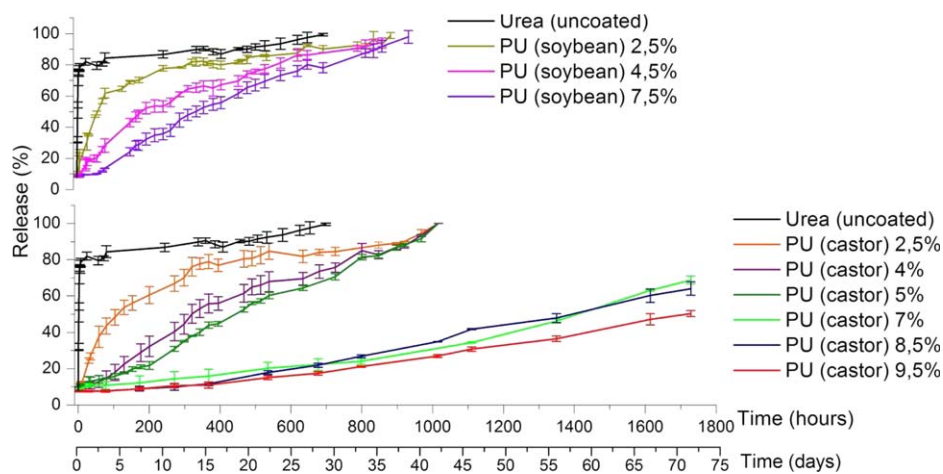
Figure 13. Water-release assay of the urea in different encapsulation polymers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

These comparisons between the curves and the release behavior were interpreted from a model modified from that suggested by Peppas to obtain the release process kinetic parameters[26]:

$$\frac{M_t}{M_\infty} = k(t - t_0)^n$$

where t is the time; k is the diffusion constant, which depends on the type of material and the permeation medium; n is the diffusional exponent, which gives information about the type of transport mechanism for a given solute; and M_t and M_∞ are the urea mass released at a time t and at the steady state, respectively. This relationship should be applied until the release reaches approximately 60%, because under these conditions, the material release behavior is an ascending straight line over time. After this period, as the release tends toward equilibrium, that is, undergoes practically no significant variation over time, the straight line slope is zero. Thus, to obtain the n and k values, graphs of ln M_t/M versus ln(time) for each release test were made, coefficients n and k being obtained from the angular coefficient and linear coefficient of the straight line, respectively.

The n parameter (diffusion process) may typically range from 0 to 1, where values of 0.5 correspond to a diffusional release through a semipermeable membrane, whereas for n values tending to 1 characterize a zero-order kinetic process. This is commonly interpreted as a process where the diffusion barrier (i.e., the coating) is dynamically changing the pore sizes or the chain organization, thus interfering in the process by retarding the expected release. It should also be noted that processes whose n value is greater than 1 indicate that the release is highly retained by the polymeric barrier, so that the total dissolution of the nutrient into the medium occurs in an infinite time.[27] Thus, the results obtained are shown in Table III, also noting the initial release time, that is, the material retention time for release (t_0).

The values obtained suggest that the increased thickness of the coating is directly related to t_0, in which release effectively starts. For all coated materials, the n value obtained is greater than or equal to 0.5, tending toward values above 1 in thicker materials from castor oil. It may be interpreted that these values indicate that the diffusion occurs from the pores in the coating, which

gradually become modified by the diffusion process itself. Therefore, for these cases it is considered that the system behavior is non-Fickian, tending (in the coated materials with PU from castor oil above 7%) toward a statistically identical behavior, governed by the constant permeation through the PU membrane. From Table III, a certain equilibrium of the coating conditions it is noted employing 7.5% soy PU and 4% castor oil PU, because both the diffusional process and t_0 are significantly close.

This characteristic shows that the same protection process can be achieved using smaller amounts of the polymer as well as diffusion barrier superiority of the polymers formed from the castor oil polyols. As seen by XRD and NMR characterizations, the higher polymerization degree obtained on castor oil samples leads to a more amorphous material, possibly with a more regular coating structure. Another important aspect is t_0, which was very long for castor oil-based PUs. This is also indicating that the coating, despite with similar thickness, has lower permeability, which is also related to the higher polymerization degree. Then, it is possible to conclude that the polymerization degree, especially in a ramificate polymer (as expected for these PUs), is playing a major role in release kinetics and time. Also, it

Table III. Calculation of the Kinetic Parameters According to the Peppas Model

Material	$k \times 10^{-3}$ (h^{-1})	n	t_0 (h)	t_0 (days)
Urea	438.0	0.38 ± 0.04	0	0
Soybean 2.5%	63.1	0.51 ± 0.02	2	0.08
Soybean 4.5%	36.0	0.49 ± 0.02	4	0.16
Soybean 7.5%	7.10	0.72 ± 0.04	24	1.00
Castor 2.5%	46.1	0.50 ± 0.02	2	0.08
Castor 4.0%	8.29	0.70 ± 0.03	30	1.25
Castor 5.0%	5.63	0.73 ± 0.04	58	2.42
Castor 7.0%	0.11	1.24 ± 0.04	291	12.12
Castor 8.5%	0.11	1.57 ± 0.05	291	12.12
Castor 9.5%	0.16	1.16 ± 0.03	291	12.12

should be noted from Table III and Figure 13, that the coating on the granules surface presents an optimum range of functionality. This is observed for materials with thicker coatings, in which the increase in polymeric coating hardly interferes with the retention gain.

In summary, the kinetic models describe that PU coatings acted as separation membranes over urea granules, driving the release process by diffusion trough the coating. The efficiency of this process is directly related to the interface quality, that is, better coating adhesion implied in longer release times. This is noteworthy that castor oil, by its specific properties, was more efficient to produce regular coatings, giving that lower thickness were able to produce very long release times. It was possible to prepare coated urea granules with PUs from plant origin polyols (soybean and castor bean), where it was observed that it is possible to control the release behavior for periods greater than 40 days under immersion in water. Castor oil polyol showed better performance in all analyses, suggesting its use in significantly reduced amounts (ca. 2.5 to 4% of urea mass). The analysis of the release kinetics suggests that the process takes place by permeation of the urea through the formed film, without necessarily having mechanical damage to the films, the film thus acting as a membrane permeable to the compound. These results can contribute to the design of more effective urea-release control systems, while preserving maximum amounts of the compound, and consequently the nutrient of interest, within the granule.

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