


Controlled-release fertilizer based on poly(butylene succinate)/urea/clay and its effect on lettuce growth

V. A. R. Baldanza,¹ F. G. Souza Jr. ,^{1,2} S. T. Filho,³ H. A. Franco,³ G. E. Oliveira,² R. M. J. Caetano,⁴ J. A. R. Hernandez,⁵ S. G. Ferreira Leite,⁵ A. M. Furtado Sousa,⁶ A. L. Nazareth Silva^{1,4}

¹Instituto de Macromoléculas Professora Eloisa Mano, Universidade Federal do Rio de Janeiro, CT, Avenue Horácio Macedo, 2030, bloco J, Rio de Janeiro, Brazil

²Programa de Engenharia Civil, COPPE, Centro de Tecnologia - Cidade Universitária, Universidade Federal de Rio de Janeiro, Avenue Horácio Macedo, 2030, bloco I, Rio de Janeiro, 21941-450, Brazil

³Instituto Federal do Rio de Janeiro - IFRJ - Laboratório Multidisciplinar de Tecnologia Agroambiental - Campus Pinheiral, Pinheiral, Rio de Janeiro, Brazil

⁴Programa de Engenharia Ambiental, Escola Politécnica, CT, Universidade Federal do Rio de Janeiro, Avenue Athos da Silveira Ramos, 149, Bloco A, Rio de Janeiro, 21941-909, Brazil

⁵Escola de Química, Universidade Federal do Rio de Janeiro, CT, Avenue Athos da Silveira Ramos, 149, Bloco E, Rio de Janeiro, 21941-909, Brazil

⁶Instituto de Química, Universidade do Estado do Rio de Janeiro, R. São Francisco Xavier, 524, Rio de Janeiro, 20550-900, Brazil
Correspondence to: F. G. Souza (E-mail: fgsj@ufrj.br).

ABSTRACT: Controlled-release fertilizer is one of the most critical tools in agribusiness for decreasing environmental impacts. Thus, the development of bio-based systems able to induce the slow release of fertilizers has become the focus of numerous researchers. In this sense, this work presents a slow-release fertilizer prepared by melt mixing of poly(butylene succinate) filled with 30 wt % urea and 5 wt % montmorillonite clay. The obtained materials were characterized using FTIR, XRD, and SAXS. Also, the release of urea was investigated using gravimetric and spectrophotometric tests. Finally, a vegetable growth analysis was performed to evaluate the development of lettuce (*Lactuca sativa* L.). The best composite material can increase the diameter of the lettuce by 67%, whereas the conventional use of urea increased this diameter by 48%. Therefore, the presented materials are useful as fertilizer systems. © 2018 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2018**, 135, 46858.

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INTRODUCTION

The world population has reached 7.5 billion.^{1,2} Specifically, 70.2% of the world population lives in the top 20 largest countries (China, India, United States, Indonesia, Brazil, Pakistan, Nigeria, Bangladesh, Russia, Mexico, Japan, Ethiopia, Philippines, Vietnam, Egypt, D.R. Congo, Iran, Germany, Turkey, and Thailand). Among them, 36.3% lives in China (18.4%) and India (17.9%).³ Most of them are expected to live a poverty life, even facing starvation.⁴ Alternatives to mitigate this almost hopeless situation must pass through new technologies, such as the use of integrated pest management,⁵ genetically modified crops,⁶ new biocontrol techniques⁷ including bioremediation of degraded areas,⁸ and the smarter use of fertilizers.⁹

Healthy plant growth depends on the number of nutrients and water available. Thus, the rational use of water resources and fertilizers is a crucial premise for agribusiness.¹⁰ However, the use of fertilizers also can generate severe environmental degradation,

such as the eutrophication of water environments.^{11–14} Thus, new ways to spread up these fertilizers, promoting their more rational use, are more and more pursued.

Among alternatives, the use of polymer systems as slow-release fertilizers or biocidal materials is promising.^{15–19} Polymers can be used as a shell^{20–22} or as a matrix²³ where the active substance is dispersed. Several petrochemical polymers have already been used to reach this purpose, such as polyethylene^{24–26} and polyamide.²⁷ On the other hand, the use of biopolymers is increasing^{28–32} because they are environmentally friendly and biodegradable.^{33–39} Besides that, their production usually consumes CO₂.^{40–42} Several examples can be cited, such as chitin,⁴³ poly(lactic acid),⁴⁴ cellulose acetate,⁴⁵ starch,⁴⁶ and more incipiently poly(butylene succinate) (PBS).^{47–50} This polymer is obtained by the polycondensation of 1,4-butanediol and succinic acid.^{48,51–60} PBS is an aliphatic, thermoplastic, and crystalline polyester with excellent thermal and mechanical properties.⁶¹ Nowadays, succinic acid can be efficiently produced from

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renewable biomass, such as crop stalk wastes, by batch fermentation⁶² also helping to remove CO₂ from the atmosphere.⁶³ Besides that, because of new biotechnological routes used in the preparation of succinic acid, this polymer is now considered as a platform material,^{64,65} and as its price falls, PBS is increasingly used. In turn, 1,4-butanediol can be prepared from succinic acid.⁶⁶ Therefore, PBS can be obtained as a genuinely green biomaterial. Also, PBS presents excellent biodegradability in soil because of the action of moisture and microorganisms. On the other hand, clay-loaded PBS composites present a smaller resistance to the water penetration, changing the biodegradability of the material.²³

Controlled-release fertilizer products are commercially prepared by coating the soluble nutrient with a membrane, often of sulfur, which serves as a barrier to diffusion.⁶⁷ In this specific context, the literature shows that PBS can be useful to produce a coating layer of the fertilizer.⁶⁸ Despite the success of the encapsulation, after the breakup of the cells, the batch leaching of the fertilizers follows the natural way of a highly water-soluble species. For this reason, the melt mixing of the fertilizer and polymer is a better way to entrap the hydrophilic filler inside the hydrophobic matrix, allowing a slower release of the fertilizer in comparison with the one from core-shell structures. So, this work presents, for the first time, the preparation and characterization of a PBS/urea/montmorillonite clay material. This material was also never tested as a slow-release fertilizer system in lettuce (*Lactuca sativa* L.), which is the main leafy vegetable crop in Brazil.⁶⁹ Thus, this work presents a slow-release fertilizer prepared by melt mixing of PBS filled with 30 wt % urea and 5 wt % montmorillonite clay. The obtained materials were characterized using several techniques. Among them, the release of urea was investigated, and a vegetable growth analysis was performed to evaluate the development of lettuce. The best composite material can increase the diameter of the lettuce by 67%, whereas the conventional use of urea increased this diameter by 48%. Therefore, the obtained results allowed us to infer that the presented composite was superior to urea, producing a faster and improved growth of the plant in comparison with pure urea.

EXPERIMENTAL

Materials

Poly(1,4-butylene succinate), Lot#MKBQ7938V, was purchased from Sigma-Aldrich (Rio de Janeiro, Brazil) at analytical grade. Urea and montmorillonite clay (Nanolite EP 25 Cod. E/163/12) were donated by the BF-Clay company (São Paulo, Brazil). All materials were used as received.

Preparation of the Polymeric Systems

Torque-versus-time measurements were carried out in a Haake PolyLab System Rheomix OS with roller rotors. The temperature for mixing was set at 125°C, and a rotor speed of 20 rpm was employed. A mixing time of 10 min was set for neat PBS and its compositions. The granules of PBS, urea, and the clay were inserted into the mixer chamber under predefined contents. The same procedure was used for the preparation of four different materials: (i) neat polymer (PBS), (ii) PBS filled with 30 wt % urea (PBS30U), (iii) PBS filled with 5 wt % clay (PBS5C), and (iv) PBS filled with 30 wt % urea and 5 wt % clay PBS30U5C.

The produced materials were frozen in liquid nitrogen, and then they were milled using an IKA bench mill, model A11. Also, in the case of the passive urea release tests, the systems were pressed in a Carver press at a temperature of 70°C under 5 MPa.

Characterization

Fourier Transform Infrared Spectroscopy Using Attenuated Total Reflectance (FTIR-ATR). FTIR-ATR analyses were performed in a Perkin-Elmer 1720X Fourier transform spectrometer. The FTIR spectra were obtained using ATR (diamond crystal) in an inert atmosphere, with a resolution of 4 cm⁻¹ in the range 4000–675 cm⁻¹. Stored results were averages of 124 scans.

X-ray Diffraction (XRD). XRD experiments were performed using a Bruker-D4 Endeavor diffractometer in a 2θ range from 4 to 80° by the fixed-time method. The steps used were equal to 0.02° with a time of 1 s, and a tube voltage and current equal to 30 kV and 15 mA, respectively, were used. The radiation used was CoKα = 1.79 Å.

Small-Angle X-ray Scattering (SAXS). SAXS measurements were performed with the beamline of the Brazilian Synchrotron Light Laboratory (LNLS, Brazil D11A–SAXS1–20160027). The distance between sample and detector was equal to 890.86 mm, allowing a q range between 0.15 and 4.64 nm⁻¹.

Scanning electronic microscopy (SEM). The morphology of the materials was determined using a scanning electronic microscope from Hitachi model TM3000, under vacuum with a secondary electron detector (Everhart-Thornley detector) and a voltage of 20 kV.

Release Tests. Batch leaching. For each test, 1 g of the material was studied using the USP Apparatus I at 75 rpm. The released amount of urea was studied in water (900 mL). All these tests were performed in triplicate. These samples were collected for quantitative analysis of urea after 0, 6.3, 12.5, 25, 52, 77, 98, and 120 h.

Sequential leaching. For each test, 1 g of the material was milled and added into a burette. This glass was plugged with cotton wool, aiming to prevent the loss of the tested release system. Known volumes of water were then added to the system. First, five 10 mL aliquots and then five 50 mL aliquots (a total of 300 mL of water) were percolated through the sample. These samples were also collected for quantitative analysis of urea.

Urea quantification. In all the cases, urea concentration was determined by an enzymatic colorimetric method using a commercial kit (Urea 500, DOLES®). The absorbance values were obtained using a Biospectro spectrophotometer at 600 nm.

Terrestrial plant growth test. Plant growth tests were used to compare the development of lettuce (*L. sativa* L.). The experiment was carried out at the Federal Institute of Rio de Janeiro (IFRJ) – Pinheiral Campus, in the south of the state of Rio de Janeiro, located at 22°30'46" South and 44°00'02" West, at 345 m altitude with regard to the sea level. Fifteen simple soil samples were collected and mixed according to procedures described by



Figure 1. (a) Lettuce seedlings in triplicate for each treatment and (b) the same lettuce crops, after 45 days, at harvest point. The experimental dynamics followed an entirely randomized design performed in triplicate. [Color figure can be viewed at wileyonlinelibrary.com]

Brazilian Agricultural Research Corporation (Embrapa).⁷⁰ The experimental dynamics followed an entirely randomized design performed in triplicate.⁷¹ There were six tested treatments: control without fertilization (T0), PBS (T1), PBS30U (T2), PBS5C (T3), PBS30U5C (T4), and urea @ 30 kg N ha⁻¹ (T5). The planting was performed on August 13, 2016, using plastic pots of 4.5 L capacity and filled with 3.5 kg of soil, and the transplanting of the lettuce seedlings of the cv Regina of the company Feltrin was performed 30 days after sowing. In every single case were used three seedlings of 4 cm height. The plastic pots were kept in a greenhouse at the IFRJ campus, as shown in Figure 1(a).

The plants were irrigated daily to maintain humidity at 60% for the whole cycle. The plants were harvested close to the cultivation soil, 45 days after planting [see Figure 1(b)].

Then, some physical evaluations were performed, such as the determination of head diameter and stem length. The means of the variables obtained in the treatments were compared using Tukey's test at 5% probability using the BioEstat 5.0 program.

RESULTS

Preparation of the Polymeric Systems

Figure 2 shows the torque values as a function of time at 20 rpm. Torque-versus-time curves provide an interpretation of the processing characteristics, reflecting the resistance of the material when subjected to certain shear stress during the mixing process.

The torque–time curves give an equilibrium torque value, which graphically depicts the melt behavior. The convergence of the torque curve to an equilibrium value indicates the complete melt of the components and also shows when the filler reached maximum dispersion.

During the first few minutes, the component granules offer resistance to the rotor rotation, and therefore, an increase in torque values is observed. When this resistance is overcome, the torque values decrease and then reach a steady-state value, which is related to the melt viscosity.

The stabilized torque results show that the urea addition into the PBS matrix led to an increase in torque values concerning torque

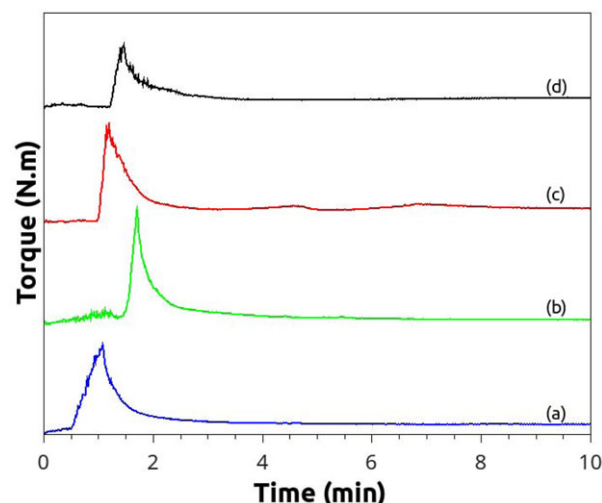


Figure 2. Torque versus time of the (a) PBS, (b) PBS5C, (c) PBS30U, and (d) PBS30U5C. [Color figure can be viewed at wileyonlinelibrary.com]

values of the neat PBS, indicating an interaction between the components. Beyond this, the homogenization time of the PBS30U blend is higher when compared to neat PBS and the other compositions. On the other hand, the addition of clay into the PBS matrix led to a decrease in torque values, indicating the effect of the filler in the induction of the flow behavior of the PBS matrix.

An interesting rheological behavior can be observed in the PBS30U5C composition. The mixing of the three components led to the lowest torque values up to around the first 5 min. This behavior suggests that the addition of clay affects the interaction between the PBS matrix and urea. For a more extended processing time, a slight increase in torque values of the PBS30U5C composite was noticed.

Figure 3 shows the specific energy values as a function of time at 20 rpm.

One can observe that the PBS30U blend presents the higher specific energy values after approximately 5 min of mixing, showing

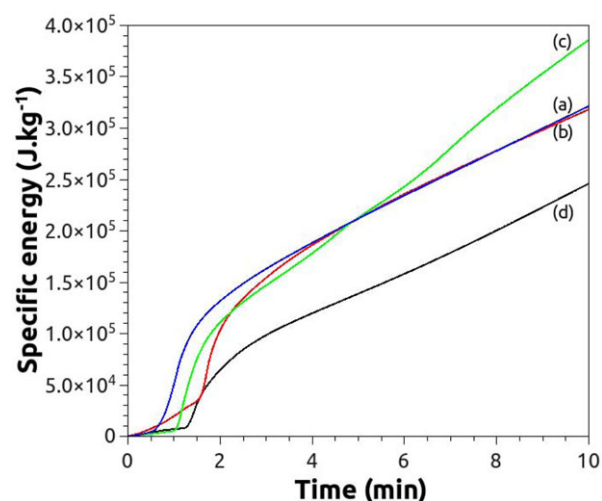


Figure 3. Specific mechanical energy of the (a) PBS, (b) PBS5C, (c) PBS30U, and (d) PBS30U5C. [Color figure can be viewed at wileyonlinelibrary.com]

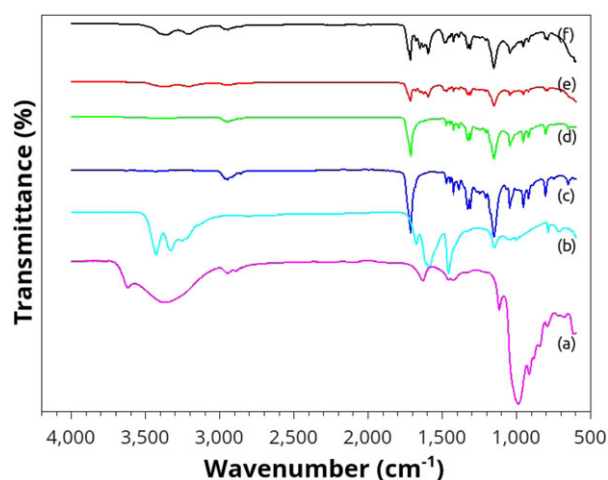


Figure 4. FTIR of (a) montmorillonite, (b) urea, (c) PBS after melt mixing, (d) PBS5C, (e) PBS30U, and (f) PBS30U5C. [Color figure can be viewed at wileyonlinelibrary.com]

the high interaction level between urea and PBS matrix. On the other hand, the PBS30U5C composite shows the lowest energy values, indicating that the energy consumption necessary to the production of the PBS30U5C composite is lower when compared to neat PBS and the other compositions. This fact suggests that the presence of the clay hinders the interaction between matrix and urea, favoring the flow behavior of the system.

Characterization

FTIR–ATR. Figure 4 shows the FTIR spectra of the tested materials. The FTIR spectrum of the montmorillonite clay is shown in Figure 4(a). This spectrum presents a band at 3617 cm^{-1} related to the nitrogenated impurities and at 3367 cm^{-1} associated with structural hydroxyls of the clay. The doublet observed at 2889 and 2944 cm^{-1} corresponds to the stretching of the CH bond from CH_3 and CH_2 groups, whereas the angular deformation from this bond appears at 1461 cm^{-1} . The characteristic band at 1632 cm^{-1} is attributed to the angular deformation of the N–H bond.

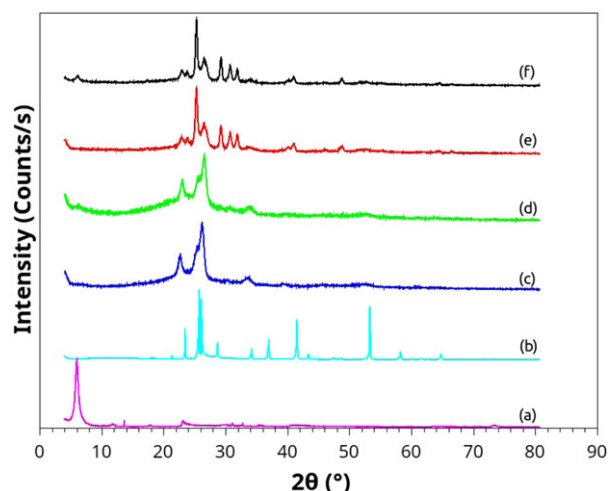


Figure 5. XRD patterns of (a) montmorillonite, (b) urea, (c) PBS after melt mixing, (d) PBS5C, (e) PBS30U, and (f) PBS30U5C. [Color figure can be viewed at wileyonlinelibrary.com]

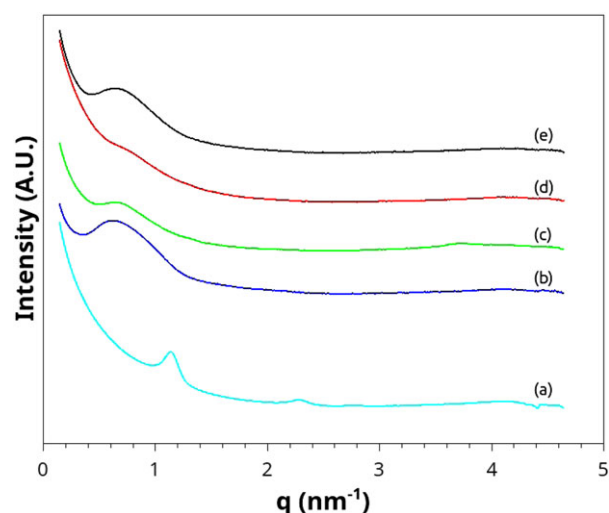


Figure 6. SAXS patterns of PBS (a) before and (b) after melt mixing, (c) PBS5C, (d) PBS30U, and (e) PBS30U5C. [Color figure can be viewed at wileyonlinelibrary.com]

The sizeable characteristic band at 989 cm^{-1} is associated with the Si–O bond. The presence of the ammonium and the CH bond from CH_3 and CH_2 groups is evidence of some organophilicity characteristics of the clay, as expected for a commercial organophilic clay.⁷² The FTIR spectrum of urea is shown in Figure 4(b), where its main peaks can be seen. Among them, for instance, NH out-of-phase stretching at 3429 cm^{-1} ; NH in-phase stretching at 3333 cm^{-1} ; C=O stretching vibrations at 1675 cm^{-1} ; N–H bending deformation at 1590 cm^{-1} ; N–H angular deformation at 1621 cm^{-1} ; C–N symmetric and asymmetric axial deformation at 1455 and 1054 cm^{-1} , respectively; and C–N angular deformation at 714 cm^{-1} .⁷³ were observed. The PBS spectrum is shown in Figure 4(c). The bands at 1321 and 2947 cm^{-1} are attributed to the symmetric and asymmetric deformational vibrations of the CH_2 groups in the main chain of PBS, respectively. The bands around 1152 and 1253 cm^{-1} correspond to stretching of the –COC– bonds in the ester group.⁷⁴ The band at 1713 cm^{-1} is related to stretching vibrations of the ester group in PBS, specifically in the C=O bonds of the carbonyl. The peaks in the 1045 cm^{-1} region are related to the stretching vibrations of O–C–C bonds in this polymer.³⁴ Peaks in the region of 3430 cm^{-1} are assigned to the terminal hydroxyl group in PBS. It is also possible to notice a band at 919 cm^{-1} corresponding to vinyl groups. The occurrence of terminal vinyl groups is attributed to the degradation reaction of the PBS chain.⁷⁵ The PBS5C is shown in Figure 4 (d). Two very tiny bands appear at 3619 and 3418 cm^{-1} at close intervals to those occurring with clay (3621 and 3367 cm^{-1}). Therefore, they are associated with the presence of the clay. In turn, the PBS30U spectrum shown in Figure 4(e) presents two intense bands at 3429 and 3330 cm^{-1} , which are related to the presence of urea. Finally, the spectrum of PBS30U5C is shown in Figure 4(f) presents the main peaks of the clay, urea, and PBS, proving that the composite material was obtained.

XRD. Figure 5 shows the XRD pattern of PBS, composites, urea, and clay. PBS before and after melt mixing presents the same characteristic peaks centered at 2θ values equal to 22.9 ± 0.2 ,

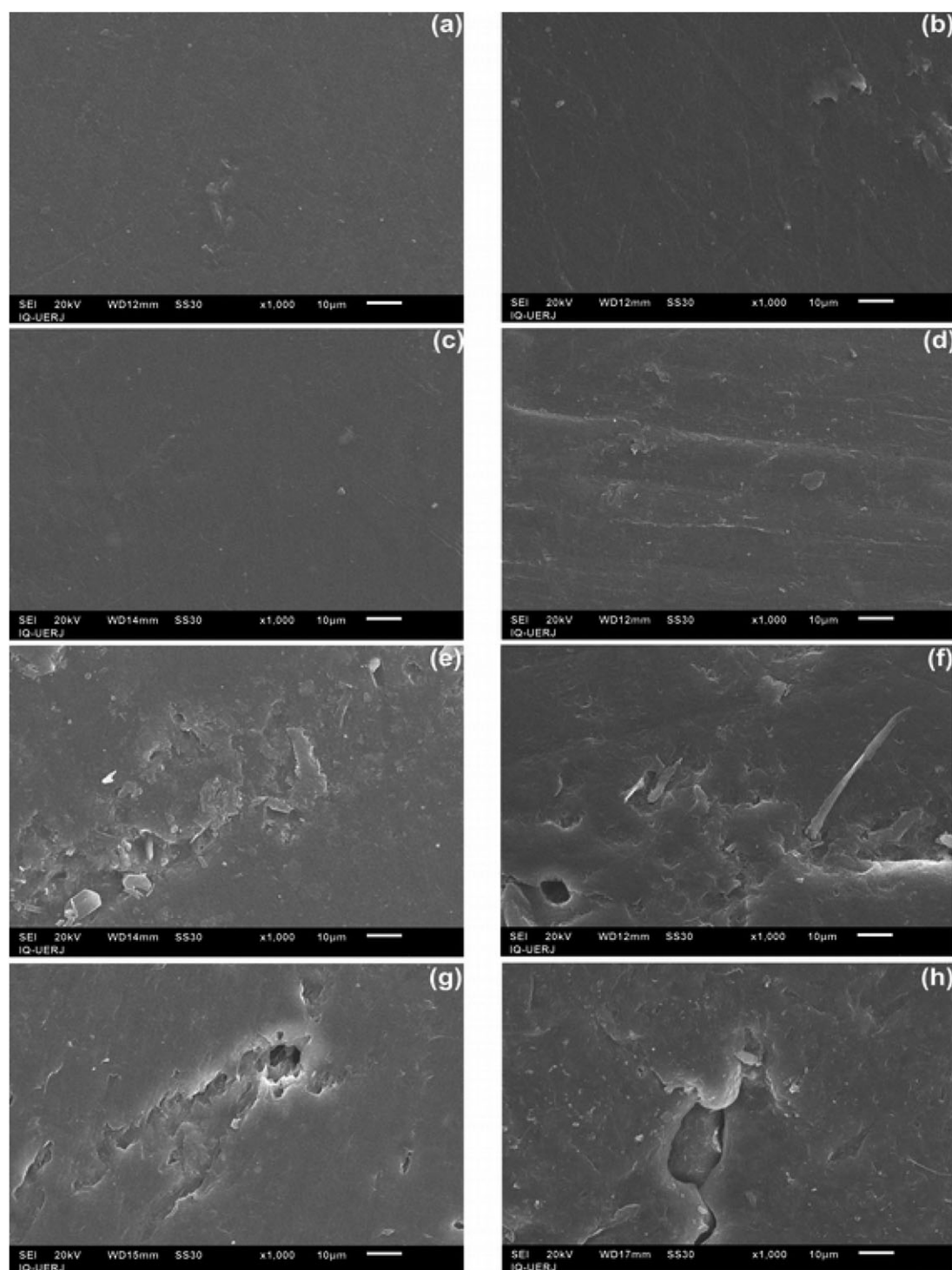


Figure 7. SEM of the samples (a,b) PBS, (c,d) PBS5C, (e,f) PBS30U, and (g,h) PBS30U5C (left) before and (right) after leaching.

25.6 ± 0.2 , 26.6 ± 0.3 , and $34.1 \pm 0.1^\circ$. These peaks correspond to the (020), (021), (110), and (111) crystalline planes in a monoclinic cell.⁷⁶ In turn, urea presented its main peaks centered at 18.5 , 21.3 , 23.7 , 25.9 , 28.8 , 34.3 , and 37.0° . These peaks correspond to the (110), (111), (102), (311), (112), (502), and (121) crystalline planes in a tetragonal cell.^{77–79} The clay before and after the melt mixing presented its main peak at $5.82 \pm 0.01^\circ$, which corresponds to an interplane distance equal to

0.883 ± 0.002 nm. Thus, the mixing processes did not affect the physical characteristics of the clay. Finally, composite materials presented characteristics peaks of the used fillers and matrix, proving the insertion of the clay and urea in the materials.

SAXS. Figure 6 shows the SAXS of the tested samples. SAXS of PBS was deconvoluted into three peaks centered at 1.14 , 2.28 , and 2.77 nm⁻¹. Aiming to understand the morphology of the

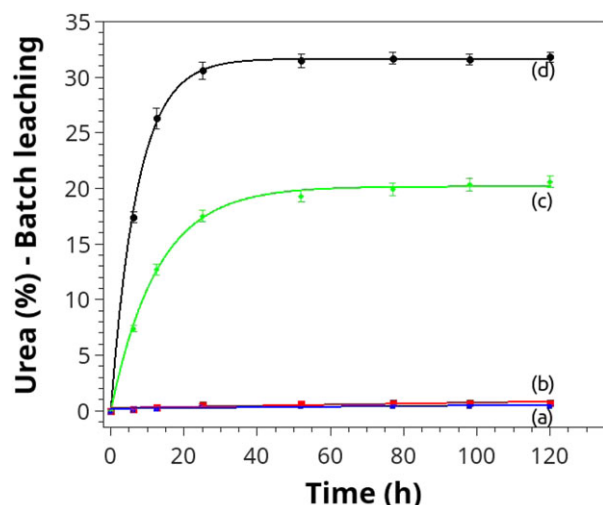


Figure 8. Urea release by batch leaching of the samples (a) PBS, (b) PBS5C, (c) PBS30U, and (d) PBS30U5C. [Color figure can be viewed at wileyonlinelibrary.com]

polymer, obtained data were compared to results that describe typical crystalline models.

The tested models were as follows: orthorhombic [q , $(13/3)^{1/2} q$, $(5)^{1/2} q$, $(16/3)^{1/2} q$], face centered cubic (CFC) [q , $(4/3)^{1/2} q$, $(8/3)^{1/2} q$, $(11/3)^{1/2} q$], body centered cubic (BCC) [q , $2^{1/2} q$, $3^{1/2} q$], gyroid [q , $(8/3)^{1/2} q$], hexagonal [q , $3^{1/2} q$, $4^{1/2} q$], and lamellae [q , $2q$, $3q$].³⁷ Among them, the unique system with $p < 0.05$ was hexagonal. As one can see in Figure 6, the melt mixing process destroys the long period organization of the matrix. Thus, the fillers are well dispersed in the matrix, and their diffusion is supposed to follow a slow-release mode.

SEM. A preliminary leaching test was performed. Then, the materials were studied by SEM before and after the leaching procedures. The obtained results are shown in Figure 7.

SEM of the PBS before [Figure 7(a)] and after [Figure 7(b)] leaching show no modifications. The same took place for the PBS5C samples. In turn, samples containing urea presented remarkable changes on their surfaces after leaching. In both cases, materials' surfaces became rougher and imperfect. These results prove that urea is present and can be removed from the material when in contact with water.

Release Tests. Urea release was tested using a standard batch leaching test. Also, a sequential leaching test was performed. The results are shown in Figures 8 and 9, respectively.

Figure 8 shows that PBS and PBS5C did not suffer mass changing. On the other hand, hybrid materials PBS30U [Figure 8(c)] and PBS30U5C [Figure 8(d)] presented release of urea, which can be empirically described using the exponential model shown in eq. (1):

$$\text{Urea}(\%) = y_0 + A \exp\left(\frac{-\text{Time}}{t}\right) \quad (1)$$

where y_0 is the initial release, A is the amplitude of the function, and t is the e-folding time.

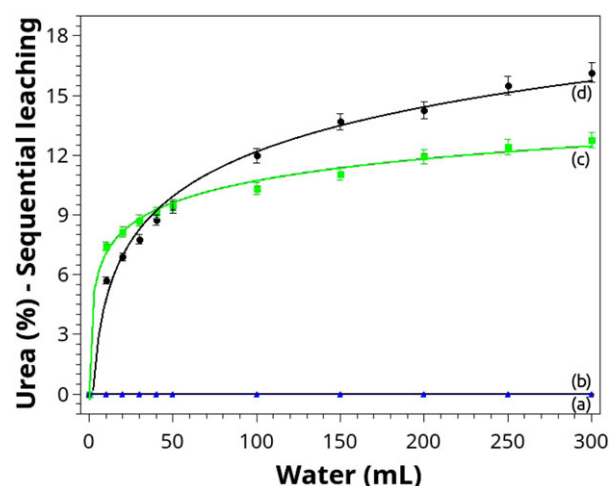


Figure 9. Urea release by sequential leaching of the samples (a) PBS, (b) PBS5C, (c) PBS30U, and (d) PBS30U5C. [Color figure can be viewed at wileyonlinelibrary.com]

In turn, Figure 9 shows again that PBS and PBS5C did not suffer mass changing during sequential leaching tests. Nevertheless, hybrid materials PBS30U [Figure 9(c)] and PBS30U5C [Figure 9(d)] presented a release of urea, which cannot be described using the exponential model. Actually, this data set can be empirically described using a logarithm model, which is shown in eq. (2):

$$\text{Urea}(\%) = y_0 + A x \log\left(\frac{\text{Volume}}{t}\right) \quad (2)$$

where y_0 is the initial release, A is the amplitude of the function, and t is the logarithm analogous to the e-folding time.

Results obtained from both models are shown in Table I. The acquired data allowed inferring that batch leaching test leads to the exhaustion of the entrapped urea in PBS30U after 40 h. After this, all the urea was released from the PBS30U system. On the other hand, at the same time, the PBS30U5C system released 64% of the total entrapped urea. Thus, the composite allowed a slower release in comparison with the system PBS30U, which is fundamental to extending the useful life of the fertilizer system.

Also, data from batch leaching could allow determining the urea release mechanism. This knowledge may be critical to tuning the desired characteristics of the fertilizer systems. Because of the high solubility of urea, Peppas' model, shown in eq. (3),⁸⁰ was used. This model was developed for a soluble drug, being used to describe the release of urea as well.⁸¹ Besides that, Peppas' model allows knowing whether the predominant mechanism is the diffusion (Fickian) or the relaxation of the chains of the polymeric matrix.⁸⁰

$$\frac{M_t}{M_\infty} = k_1 x t^m + k_2 x t^{2m} \quad (3)$$

where M_t/M_∞ is the fraction of urea released, m is the release exponent depending on system geometry (here, m is equal to 0.58), k_1 and k_2 are the Fickian and relaxational contributions, respectively, and t is the release time.

The percentage of urea released due to the Fickian mechanism, F , can be calculated according to eq. (4).⁸²

Table I. Urea Release Parameters from Batch Leaching and Sequential Leaching Data

| Parameter | Batch leaching (exponential model) | | Sequential leaching (logarithm model) | |
|-----------|------------------------------------|-------------------|---------------------------------------|-----------------|
| | PBS30U | PBS30U5C | PBS30U | PBS30U5C |
| A | -20.16 ± 0.51 | -31.67 ± 0.14 | 3.91 ± 0.35 | 7.83 ± 0.41 |
| t | 12.76 ± 1.19 | 7.30 ± 0.30 | 7.46 ± 0.31 | 4.23 ± 0.39 |
| y_0 | 20.17 ± 0.25 | 31.68 ± 0.06 | 6.31 ± 0.69 | 1.33 ± 0.32 |
| R^2 | 0.995234 | 0.999941 | 0.984830 | 0.995135 |

Table II. Average Head Diameter and Stem Length for Lettuce (*L. sativa* L.) cv Regina

| Sample | Identification code | Head diameter (cm) | Stem length (cm) |
|----------|---------------------|--------------------|------------------|
| Control | T0 | 21.33a | 1.87a |
| PBS | T1 | 22.33b | 2.63b |
| PBS30U | T2 | 36.00c | 3.80c |
| PBS5C | T3 | 27.33d | 2.63d |
| PBS30U5C | T4 | 35.67e | 4.27e |
| Urea | T5 | 31.67f | 4.07f |

Means followed by the same lowercase letter in the collumm do not differ from each other according to Tukey's test at 5% probability. Control (without fertilization), PBS (pure), PBS30U (PBS + 30% urea), PBS5C (PBS + 5% clay), PBS30U5C (PBS + 30% urea + 5% clay), urea (30 kg dose of $N\ ha^{-1}$).

$$F = \frac{1}{1 + \frac{k_2}{k_1} x t^m} \quad (4)$$

The sample PBS30U presented k_1 and k_2 values equal to 2.19 and 0.04 ($R^2 = 0.990$), respectively. In turn, PBS30U5C presented k_1 and k_2 amounts equal to 4.84 and 0.20 ($R^2 = 0.988$), respectively. Before 15 minutes, the release is controlled by diffusion. This result is expected because the urea on the surface of the particles dissolves easily. On the other hand, as time goes by, the relevance of the chains' relaxation mechanism increases. This phenomenon is more relevant in the case of the material filled with clay (PBS30U5C) because the clay affects the interaction between the polymer chains making the relaxation of the organic structure easier. More specifically, eq. (4) allowed inferring that, after 120 h, the amount of urea released from PBS30U and PBS30U5C by relaxation was equal to 23 and 41%, respectively.

In turn, the data from sequential leaching allowed inferring that the steady state of the urea release was not achieved, even after the use of 300 mL of water. For comparison, total pluviometric data from Rio de Janeiro, Brazil allowed inferring that the monthly rainfall volume in 2009 was equal to 140 ± 18 mL (Ref. ⁸³) despite the historical values only reaching 98 ± 6 mL according to INMET (Brazilian Institute of Meteorology).⁸⁴ Therefore, according to the obtained data, the presented materials can be used as fertilizer release systems by more than two years. Of course, the biodegradation capability of the tested materials will reduce this period, but this issue was not evaluated here.

Terrestrial Plant Growth Test. Finally, the lettuce plant growth was performed. The PBS, PBS30U, PBS5C and PBS30U5C samples were always tested in comparison to two controls: (i) one

without urea addition and (ii) the other using commercial urea. The obtained data are shown in Table II.

The lettuce growth tests used to evaluate the performance of the polymer systems were mean head diameter and stem length. The p value found for the treatments was always lower than 0.05. Thus, the difference between the treatments is significant. The data indicate that for the different treatments, the behavior of the variable was different. The PBS30U treatment (PBS + 30% urea) showed a better result than the others, being 12% superior to the treatment with agricultural urea and 59% higher than the control. Therefore, the PBS30U5C system is the best choice among treatments because it presented the best result in the two plant growth evaluations performed. For comparison, the literature shows that the use of biostimulation fertilizing systems based on bacterial-algal preparation led to a significantly higher lettuce weight compared to the control, equal to 22.7%.⁸⁵ In turn, the treatments with organic fertilizers increased the lettuce weight by 18%.⁸⁶ Finally, the obtained results allowed inferring that the presented composite induced an improved growth of the plant in comparison with pure urea and other systems. So, this new material is potentially useful as a fertilizer system.

CONCLUSIONS

The main results allowed inferring that the proposed composite was obtained. In turn, SAXS proved that melt mixing destroyed the extended period organization of the matrix. Thus, the fillers are well dispersed in the matrix, and their diffusion is supposed to follow a slow-release mode. This assumption was proved by the release tests. Also, the best composite material increased the diameter of the lettuce by 67%, whereas the conventional use of urea increased the diameter by 48%. Therefore, the presented

materials can positively impact economic and environmental advantages of the lettuce crop, increasing its yield.

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AUTHOR CONTRIBUTIONS STATEMENT

M.Sc. Viviane A. R. Baldanza performed the preparation of the materials. D.Sc. Fernando G. Souza Jr. supervised the research and wrote the manuscript. D.Sc. Sérgio Thode Filho performed the statistical analysis of the Terrestrial plant growth test. D.Sc. Heider A. Franco performed the Terrestrial plant growth test. D.Sc. Geiza E. Oliveira performed the FTIR analysis. M.Sc. Rosana M. J. Caetano performed the release tests. D.Sc. Jose A. R. Hernandez performed the analysis of the release tests. D.Sc. Selma G. Ferreira Leite performed the release tests. D.Sc. Ana M. Furtado Sousa performed the melt mixing tests. D.Sc. Ana L. Nazareth Silva performed the analysis of the melt mixing tests.

DECLARATIONS OF INTEREST

None.

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