



A Novel, Simple Route to Produce Urea:Urea–Formaldehyde Composites for Controlled Release of Fertilizers

A. S. Giroto^{1,2} · G. G. F. Guimarães² · C. Ribeiro²

Published online: 15 November 2017
© Springer Science+Business Media, LLC, part of Springer Nature 2017

Abstract

Nitrogen loss through NH_3 volatilization is a primary concern for urea as fertilizer due its fast hydrolysis by soil urease. To minimize this problem herein we developed a partially-polymerized urea–formaldehyde granule as a slow-release fertilizer, by melt stage process as a viable route for large-scale production. In this product the unreacted urea fraction acts as a fast release nutrient source while the polymerized fraction acts in longer times depending on the polymerization degree. This characteristic was analyzed by means of soil incubation experiments (up to 42 days), where the available NH_4^+ contents along time indicated significant lower N losses compared to conventional fertilizer, even for low-polymerized materials. Residual N in the structure was kept stored in the soil for future use by plants, as desired in many agricultural practices, showing that this simple polymerization method provides a smart fertilizer controlled by chemical structure.

Keywords Nitrogen losses · Partial polymerization · Controlled-release · Fertilizer

Introduction

Urea is one of the main sources of N used due to its high concentration (46% N) that allows concentrated formulations at lower costs compared to other sources [1]. However, this fertilizer shows less efficiency than other nitrogen sources for a large number of crops in different soils and climates, due to different causes, such as NO_3^- leaching, NH_3 volatilization, and its toxic effect on the plants at the beginning of the vegetative period [2–4]. These factors not only contribute to reducing the efficiency of urea, biomass production, and economic cultivation but also are an important source of environmental pollution.

One of the alternatives to reduce these losses is to reduce urea hydrophilicity, allowing its application as slow release fertilizers. In this scenario, urea formaldehyde (UF) was the first synthetic nitrogen fertilizer produced with low solubility and it belongs to the first group of materials specially

developed on a commercial scale for the slow release of nitrogen [5–7]. Studies have verified that N-release from an organic polymer occurs in stages similar to those adopted for urea in agriculture [8–10]. However, most of the research into this polymer synthesis reports the production in the liquid phase, as seen by many patents [11–15]. This process is difficult to control, generally leading to fast polymerization with poor processability. Besides that, the literature does not show strategies for partial polymerization, i.e., all the available products are based on fully-polymerized systems. Therefore, the nutrient release is often too long for practical application, meaning that the nutrient is available for longer periods than the requested by a plant growth. This fact explains why urea–formaldehyde polymers are not popular as controlled release fertilizers, despite their higher N content compared to other commercial products. In recent research from our group, we proposed a novel nanocomposite material based on the exfoliation of montmorillonite into the matrix of a urea/urea–formaldehyde polymer [6]. A remarkable aspect of this process was the use of a formaldehyde solid precursor instead of the most common formaldehyde solution. Despite its simplicity, this method was limited as to the maximum amount of urea in composition (around 80%), and by the need of partial urea solubilization for a plastic mixture. Considering the basic strategy, herein we propose to investigate the polymerization in the urea melt

✉ C. Ribeiro
caue.ribeiro@embrapa.br

¹ Department of Chemistry, Federal University of São Carlos, Washington Luiz Highway, km 235, São Carlos, SP 13565-905, Brazil

² Embrapa Instrumentation, 1452, XV de Novembro Street, CP: 741, São Carlos, SP 13560-970, Brazil

stage, by also using the formaldehyde precursor previously mixed as powders. The results showed that by this simple method it is possible to obtain dense urea:urea–formaldehyde composites, and with very high N contents (comparable to commercial products), and with nutrient release easily controlled by the composition.

Materials and Methods

Materials

Raw materials used in composite formulations were urea (Synth) and paraformaldehyde (Sigma-Aldrich). The urea was previously milled to 300 μm in a TE-330 hammer mill (Tecnal, Brazil).

Preparation of Materials

Composites were prepared with different molar ratios of urea and paraformaldehyde (Ur/Pf) as 1:1, 1:0.5 and 0.5:1, respectively. The urea–formaldehyde polymer was formed by reaction of formaldehyde with an excess of urea. In the first stage, urea is hydroxymethylated by the addition of formaldehyde to the amino groups. This reaction actually is a series of reactions that lead to the formation of mono-, di-, and trimethylolureas. The second stage of urea–formaldehyde resin synthesis consists of condensation of the methylolureas to low molecular weight polymers. The exact ratio, of course, is dependent on the reaction conditions employed in the addition reaction [6].

Paraformaldehyde is a formaldehyde polymer with a polymerization degree between 8 and 100. This polymer depolymerizes in water and heat [16]. Thus, the use of paraformaldehyde allows control of the urea solubility inside the composite by the extension of the polymerization reaction. The precursor materials (urea and paraformaldehyde) and water (9 wt%) were pre-homogenized and mixed-melted using a torque rheometer (Polylab RHEODRIVE Rheomix mixer and OS4) under the conditions of 60 rpm for 10 min at 90 °C. After mixing, the samples were cured at 80 °C in an oven for 12 h and subsequently stored at 90 °C until completely dry. The nomenclature given to each composition and the elementary composition is presented in Table 1.

Characterizations

The materials were initially characterized by scanning electron microscopy (SEM) using a JSM6510 microscope (JEOL). Samples were previously fixed onto carbon tapes and coated with thin layer of gold in an ionization chamber (BALTEC Med. 020). The imaging by SEM was carried out using the secondary electron mode. The optical

Table 1 Nomenclatures of composites, molar ratio, and their total nitrogen %

Nomenclature	Molar ratio (Ur/Pf)	Total nitrogen (%)
Urea	–	46.89
Ur/Pf 1:0.5	1:0.5	41.29
Ur/Pf 1:1	1:1	40.33
Ur/Pf 0.5:1	0.5:1	28.21

The raw materials used are identified by initial Ur for urea and Pf for paraformaldehyde

image from paraformaldehyde was done using an optical microscopy L2800 Biological Microscope (BEL Photonics, Brazil).

X-ray diffractograms (XRD) were obtained using an XRD 6000 diffractometer (Shimadzu). The relative intensity of diffraction was registered in the angular range (2θ) of 3°–40°, using a Cu K α incident beam ($k = 0.1546$ nm) and scanning speed of 1° min⁻¹ at 30 kV voltage and 30 mA current.

Thermal degradation of samples was evaluated in the 25–600 °C range using a Q500 analyzer (TA Instruments, New Castle, DE, USA) under the following conditions: sample size 10.0 \pm 0.5 mg, synthetic air atmosphere (80% N₂ and 20% O₂) with 60 mL min⁻¹ flow, heating rate of 10 °C min⁻¹. For differential scanning calorimetry (DSC), samples were heated from 25 to 300 °C under nitrogen flow of 60.0 mL min⁻¹ in a DSC Q100 (TA Instruments, USA). The linear heating rate used in both analyses was 10 °C min⁻¹.

¹³C solid-state nuclear magnetic resonance (NMR) measurements were performed on a Bruker (Karlsruhe, Germany) 400 MHz to ¹H (9.4 T) spectrometer using ¹³C cross polarization magic angle spinning (CPMAS) technique in a 4 mm broadband ¹H/X MAS probehead. The following parameters and values were used: speed spinning of 8 kHz, 90 ° ¹H pulse length of 2.3 μs , contact time 2 ms, spectral width 50 kHz, 20 Hz of line broadening, and a recycle delay of 3 s. Hexamethylbenzene (HMB) was used as external reference standard at 17.2 ppm for methyl-carbons. All the NMR experiments were carried out with 4096 scans. Fourier Transform Infrared (FT-IR) analyses were performed on a Bucker spectrometer using a spectral resolution of 4 cm⁻¹.

Evaluation of Urea Release in Water

The urea release in water at 25 °C and natural pH for each polymer was examined following a method adapted from Tomaszewska and Jarosiewicz. The total N organic content in each composite formulation was determined by elemental analysis (Thermo Finnigan Model Flash 1112EA). These

results (Table 1) were used to calculate the amount of material used in the release tests. Briefly, samples were soaked in water at 25 °C and were constantly homogenized by gentle stirring using an orbital shaker during 5 days. Pure urea was also tested as a control experiment [17]. The urea concentration in solution was determined by UV–Vis spectrophotometry in a 1601PC spectrophotometer (Shimadzu, Japan) according to the method reported by With et al. [18]. Curves of the percentage of urea-solubilized as a function of time were then obtained. The measurements were replicated three times under identical laboratory conditions for each type of composite formulation.

Release and Transformation of N in Soils

The release of urea from the composites was also evaluated in two Oxisols, both were collected in the surface (0–20 cm) in an area with agricultural activity in the municipality of São Carlos, Brazil. Before use, the soil samples were air-dry and crushed to pass through a 2 mm screen. The soil chemical and physical properties are reported in Table 2. The pH was determined with a glass electrode (soil:water ratio, 1:1); organic C by the Walkley–Black method [19]; cation-exchange capacity (CEC) [20]; soil texture analysis was determined by the pipette method [21]; water-holding capacity (WHC) [20]; and urease activity using the buffer method of Tabatabai and Bremner [22].

To compare the urea release and N transformations, soil samples were incubated with urea or composites at a ratio of soil:N (1000:1 g g⁻¹) placed in 125 mL polyethylene screw-cap bottles as Urea, Ur/Pf 1:1, 1:0.5 and 0.5:1. The samples were incorporated into the soils and soil moisture content was standardized at 80% WHC with the addition of deionized water. A container with 5 mL of 4% boric acid (Sigma-Aldrich) was added in the polyethylene bottles, to capture the volatilized ammonia (NH₃) during the incubation period. Samples were incubated for 0, 1, 3, 7, 14, 21 and 42 days under controlled air temperature and humidity.

Table 2 Chemical and physical properties of the studied soils

Oxisol	Red–Yellow	Red
pH	5.4	5.0
Organic C (g kg ⁻¹)	7.6	7.0
CEC (cmol _c kg ⁻¹)	4.8	4.2
Sand (g kg ⁻¹)	667	433
Silt (g kg ⁻¹)	19	35
Clay (g kg ⁻¹)	314	532
WHC (g kg ⁻¹)	140	200
Urease activity (mg N kg ⁻¹ h ⁻¹)	9.7	7.1

CEC cation exchange capacity, WHC water-holding capacity

Analyzes were performed after each incubation period. Determinations were carried out via volatilization of boric acid by titration with HCl 0.01 mol L⁻¹ (Synth) and then the soil mineral N was extracted by KCl 1 mol L⁻¹ (Vetec) at the extractant:soil ratio (10:1). In order to paralyze the urease activity, 5 mg L⁻¹ of phenylmercuric acetate (Sigma-Aldrich) from the extraction stage was added to the extraction solution. The suspension remained under stirring for 1 h and was then filtered with the use of a slow filter with a diameter of 12.5 cm (Nalgon). The extract was stored in a polyethylene bottle with a volume of 100 mL at 5 °C in a refrigerator.

The ammonium (NH₄⁺) and nitrate (NO₃⁻) levels in the extracted soil were analyzed by the colorimetric method [23, 24]. The contents recovered in each N fraction were expressed as percentages referring to the N applied as urea or composites. The profile of the volatilization of ammonia (NH₃) and the formation of NH₄⁺ in soil was presented by the average values accompanied by their respective standard deviations. Differences among treatments by total recovery as NH₃ volatilized and exchangeable NH₄⁺ and NO₃⁻ after aerobic incubation were assessed by analysis of variance (ANOVA) and when the F test was significant, differences among treatments were compared by the Tukey test (P < 0.05).

Results and Discussion

In previous works urea and formaldehyde were used to synthesize UF resins and the reaction was always performed in aqueous solution [11–13]. Here, in order to improve the yield and stabilization of UF resins, paraformaldehyde was used as the raw material and the reaction was performed in urea melt. This work proposes using just the mixing–melting between urea and paraformaldehyde follow by cure and drying of materials, avoiding large amounts of water in addition to acids and basic reagents used to control the reaction medium. Therefore, the data for characterization of formed polymers are presented below.

Figure 1 shows XRD patterns of the pure urea and paraformaldehyde and composites with different compositions. The pattern of neat urea and paraformaldehyde showed typical peaks at 2θ = 22.5°, 24.7°, 29.3°, 31.8°, 35.5°, 37.3° and 22.9°, 34.3° for the precursor materials, respectively. By the XRD patterns of samples, it was possible to verify the polymerization by a wide band in the reacted samples, which is characteristic of a semi-crystalline material. This band is proportional to the molar ratio of paraformaldehyde in mixtures, i.e., the polymerization is directly influenced by the amount of this compound, as expected. This is consistent with the findings for Roumeli et al. [25], who observed the highest amorphous proportion

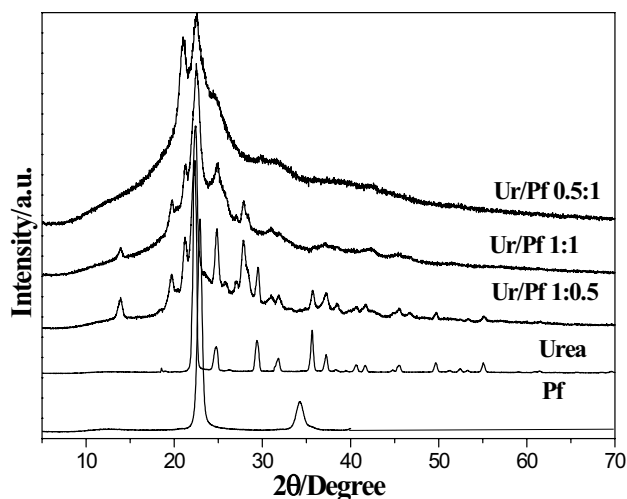


Fig. 1 XRD patterns for neat urea, paraformaldehyde, and formulations of urea/paraformaldehyde at different molar ratios

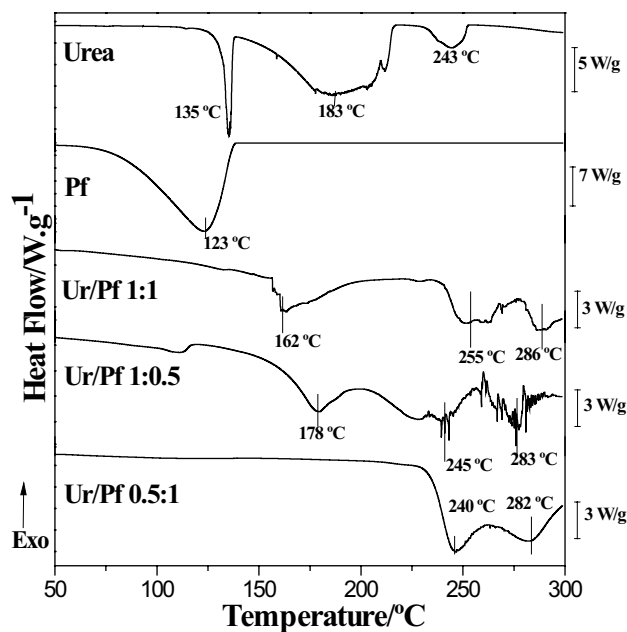


Fig. 2 DSC curves for neat urea, paraformaldehyde and polymers

in urea:formaldehyde composites at a ratio of 0.5:1 (Ur/Pf), i.e., excess formaldehyde.

DSC experiments were used to confirm the thermal behavior of the polymerization reaction among components. Figure 2 shows DSC profiles for neat components and mixtures, where the endothermic peak of paraformaldehyde at 123 °C is absent in any of the mixtures—which is an indicator that this component was totally consumed during the polymerization step, as reported by Yamamoto et al. [6]. Regarding urea, melting at 135 °C and decomposition

between $150 < T < 210$ °C are clearly seen [26]. As presented in Fig. 1 for the Ur/Pf 0.5:1 polymer (which is supposed to be a fully polymerized material, since paraformaldehyde is in stoichiometric excess), the shift to 246 and 286 °C is confirming the complete polymerization (probably associated with degradation steps). For the other samples, peaks suggesting to free urea degradation were still present (162 and 178 °C).

Figure 3 shows the TGA/DTG curves for neat precursors and polymers. This analysis confirms the polymerization degree of different samples. In the urea TGA curve, three distinct thermal events are visible, urea decomposition onset $160 < T < 210$ °C and degradation around 237 °C (loss of amine groups) and around 292 °C degradation of polymerized fractions [26]. It was also observed that paraformaldehyde shows a single mass loss step at 150 °C, which is related to a direct volatilization process—confirming that the peak at 123 °C in DSC (Fig. 2) is associated with this process. For Ur/Pf 0.5:1 sample a significant (68%) mass loss at the range 174–384 °C corresponding to depolymerization/volatilization/decomposition of Ur/Pf polymer followed by a second mass loss around 20% due to an initial degradation of the polymer chain. Considering that the proportion 0.5:1 is relative to the material more polymerized a residual of 8.54% is observed after 600 °C probably due to strong crosslinking formed between urea and formaldehyde groups in the final material. The thermal profile of sample 0.5:1 shows consequently more degradation peaks in the DTG curve, related to the presence of the urea–formaldehyde polymer. This was also seen in the Ur/Pf 1:1 sample but with a less amount of residual material (5.43%) probably owing a lower amount of urea polymerized in comparison to the previous material with a higher proportion of paraformaldehyde (0.5:1). While the material Ur/Pf 1:0.5 had no weight left after 600 °C. This was expected since Ur/Pf stoichiometry for full polymerization is at least 0.5:1, thus the others materials should be classified as urea:UF composites due to free urea still presented. However, even in these materials, DTG data reveal that the majority of the material is polymerized since the main peak weight loss is at 280 °C for all polymers. These results showed that the 0.5:1 ratio is necessary if complete urea polymerization is desired [27]. Furthermore, the results showed that Ur/Pf polymers synthesized by melt condensation polymerization have lower free formaldehyde content, high thermal stability, and better stability during storage [28].

Figure 4 shows SEM micrographs of the pure urea and obtained polymers and paraformaldehyde optical image. The urea shows regular size particles larger than 50 μm. The morphology of the Ur/Pf 1:0.5 (Fig. 4b) shows that the surface is composed of rod-shaped and fibrous crystals formed above a homogenous surface, referred to as unreacted urea. For the sample Ur/Pf 1:1, the reaction leads to large amounts

Fig. 3 TGA (a) curves and DTG (b) of Ur/Pf formulations and their neat precursors

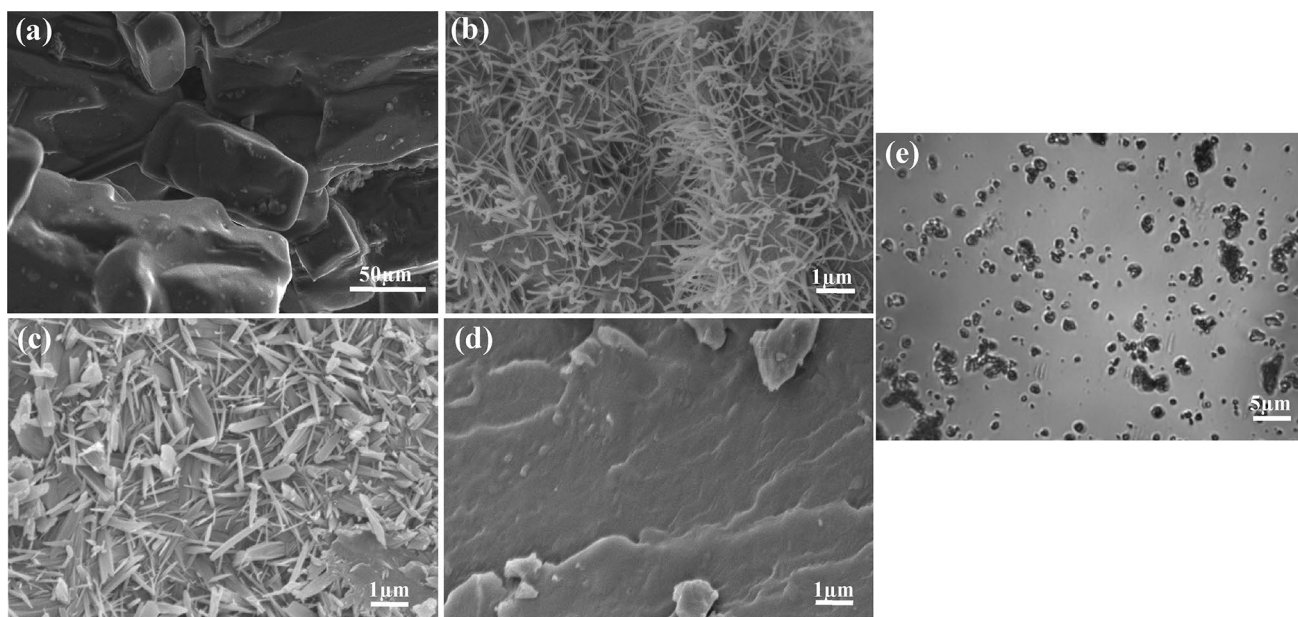
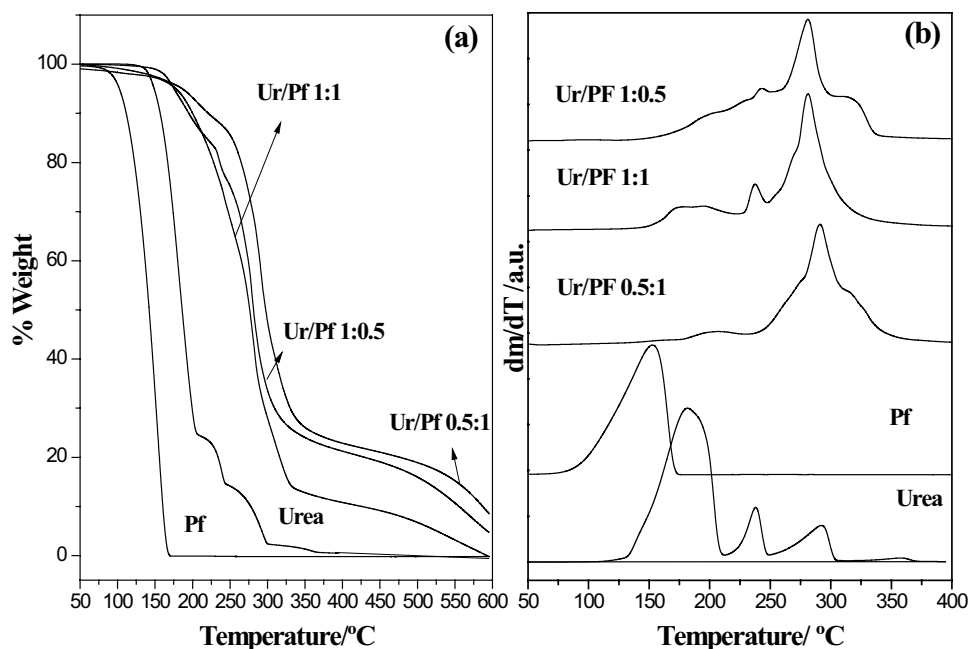


Fig. 4 SEM micrographs for **a** pure urea, **b** Ur/Pf 1:0.5, **c** Ur/Pf 1:1, **d** Ur/Pf 0.5:1 and **e** optical image from paraformaldehyde

of thicker needle-shaped particles, indicating the higher polymerization degree, as supposed. Finally, Ur/Pf 0.5:1 showed a smooth and homogeneous surface, which indicates the change in morphological evolution during polymerization—since previous results show the complete urea polymerization in this material. As observed by the optical image, the paraformaldehyde resembles small granular, near-spherical particles, whose morphology is not seen in the polymerized samples. This indicates that the needle-shaped structures are resultant of the polymerization reaction, by a

re-crystallization mechanism, and are not remnants of the precursor materials. This needle-shaped structures tend to coalesce to larger rods, leading to almost continuous phases, as seen in Ur/Pf 0.5 sample. Therefore, it may be proposed that this shape results from the formation of small seeds in liquid/dissolved phase, precipitating over urea granules. Following, the growth of needle-shape structure is defined by the preferential growth in high-energy planes, which is surpassed by isotropic growth in high crystallization extension, leading to bigger crystals by classical growth or coalescence.

This is almost similar to the crystal growth from melt, typically seen for metals and many other polymers crystallized from solution [27].

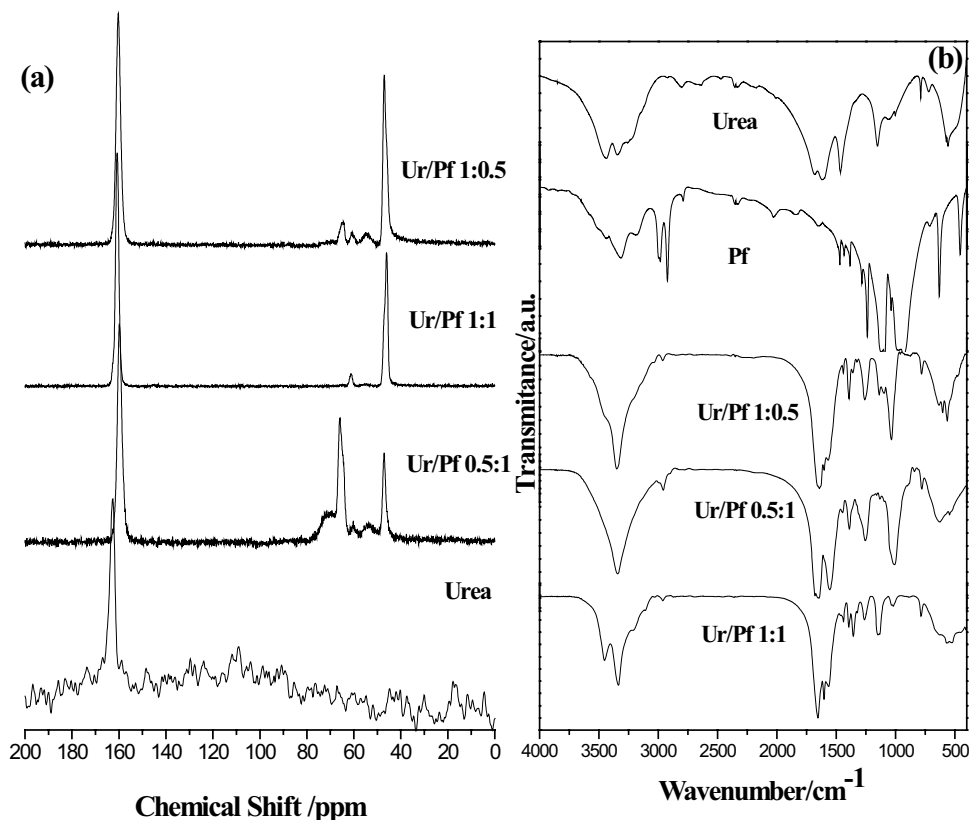
The ^{13}C NMR analyses were performed upon the synthesis of polymers in order to better understand the chemical structure formed after curing process, as seen in Fig. 5a. Based on ^{13}C chemical shifts it is possible to evaluate the presence of various functional groups on the polymers. Table 3 summarizes the chemical shifts confirming the proposed reactions. In the first step, the hydroxymethylation refers to the addition of up to three formaldehyde molecules with a urea bifunctional molecule thereby producing hydroxymethylureas, as noted by the chemical shift around 65–66 and 71–72 ppm. In some cases, hydroxymethylation conditions (slightly alkaline pH and temperatures around 70 °C) also favor the formation of methylene ether bridges between hydroxymethylureas as observed for the polymer Ur/Pf 1:1 at 76 ppm. These ether bridges may later undergo rearrangement to form methylene bridges ($-\text{CH}_2-$), thereby releasing formaldehyde molecules.

The second stage, acid condensation, epitomizes the oligomer Ur/Pf. The hydroxymethylureas, the free urea, and free formaldehyde react to form linear or partially branched molecules with average or high molecular weights. The type of bridge predominantly formed at this stage is the methylene bridge with chemical shifts around 47–48, 53–54 and

60–61 ppm as observed for all materials. In the third synthesis step, the second portion of urea reacts with the free formaldehyde producing more hydroxymethylureas. It was possible to verify the formation of species with different degrees of free urea substitution. For the chemical shifts shown there is a priority formation of mono-substituted urea for materials with the 1:1 and 1:0.5, materials with lower polymerization degrees and the formation of di-substituted urea for the polymer Ur/Pf 0.5:1, the polymer with the highest polymerization degree. This material also exhibited chemical shifts regarding branched chemical groups [27–30]. It was not observed any paraformaldehyde band left (in the region of 80–90 ppm) which is attributed to single carbon present (reactive formaldehyde oligomer) as also observed by Hoong et al., Fan et al. and Tomita et al., [31–33] showing that all paraformaldehyde was polymerized.

Figure 5b shows a comparison of FT-IR spectra from 4000 to 400 cm^{-1} between pure urea, neat paraformaldehyde, and Ur/Pf polymers. All the changes of amine stretching vibration frequency indicate the formation of Ur/Pf polymer, which was consistent with previous work [25, 27, 34]. It was possible to see that multiple and broad peaks in the Ur/Pf resin spectra are mainly due to the polymer structure complexity. The bands at 3439 and 3336 cm^{-1} correspond to N–H asymmetric and symmetric stretching of urea as shown for pure urea and Ur/Pf 1:0.5 clearly exhibit that the same

Fig. 5 **a** The spectrogram of ^{13}C NMR of urea and polymers, **b** FTIR transmittance spectra of pure urea, neat paraformaldehyde, Ur/Pf 1:0.5, Ur/Pf 0.5:1 and Ur/Pf 1:1



stretching frequency disappears and shifts to higher regions (3422 cm^{-1}) after the reaction for Ur/Pf 1:1 and Ur/Pf 0.5:1. The broad peak around $3350\text{--}3450\text{ cm}^{-1}$ can be also attributed to the hydrogen bonded O–H and N–H. The fact that this band is rather broad may be attributed to monomers such as water and formaldehyde, whose O–H group may form hydrogen bonds with reactive functional groups such as CH_2OH , NH_2 , and N–H, as observed by Jada [36]. But no band was found in the regions of $1097\text{--}905\text{ cm}^{-1}$ (C–O aliphatic ether) referent to paraformaldehyde indicating that no residue of this material was presented in final polymers [37]. Also, it is important to mention that the free --NH_2 group has a characteristic peak at 3440 cm^{-1} , while the bonded --NH group at 3340 cm^{-1} [25]. In spectra for urea, the characteristic bands of amide I, II, and III are around 1680 , 1612 and 1463 cm^{-1} , respectively. These peaks are assigned to the C–O stretching of amide I and II, as well as the N–H scissors of amide I. The multiple peaks at $1460\text{--}1470\text{ cm}^{-1}$ may be attributed to C–H bending vibrations of the $\text{CH}_2\text{--N}$ group, while the small peaks in the area of $1320\text{--}1450\text{ cm}^{-1}$ can be assigned stretching of groups like CH_2OH , CH_3 , and CN as observed also by Zhong et al. [38]. The shift has also been assigned to C–H stretching and O–H bending vibrations of alcohol, but in Ur/Pf 1:1 these peaks almost disappear. The fact that in the pure UF resin spectrum, the peak is centered at the area of 3410 cm^{-1} in the space of Ur/Pf 0.5:1, indicates that the amount of bonded --NH is higher compared to the free --NH_2 . The 1255 cm^{-1} peak is attributed to both the asymmetric stretch of $\text{N--CH}_2\text{--N}$ and the asymmetric stretch of --C--O--C-- of ether linkages [35]. Also, the peak at 2958 cm^{-1} becomes sharper and more distinct, which along with the absence of the 2900 cm^{-1} peak of the asymmetric C–H alcohol stretches, indicates that quantity of ether and methylene linkages is increased in the cured resin and thus, a cross-linking process has evolved.

Figure 6 shows the urea release profile in water (full immersion) for all samples. It is noteworthy that all materials had a slowed behavior in the urea release, even the non-completely polymerized sample (Ur/Pf 1:0.5) when compared to urea. The degree of polymerization plays a key role in this process since the release time and the equilibrium value over 50 h was directly dependent on the polymer content. It was observed that Ur/Pf 1:0.5 showed a behavior very close to pure urea. Considering that this sample is characterized by a partially polymerized structure, this release may correspond to the solubilization of that unreacted urea, but also to the polymer itself—since this is probably a low molecular weight polymer, it is possible that the structure presents some solubility and then, part of the solute correspond to oligomers or soluble polymeric chains. However, this suggests that the time for total urea release for this polymer may be greater than 120 h, i.e., 5 days of complete immersion in water. For other materials, urea releases only 30 and 20%

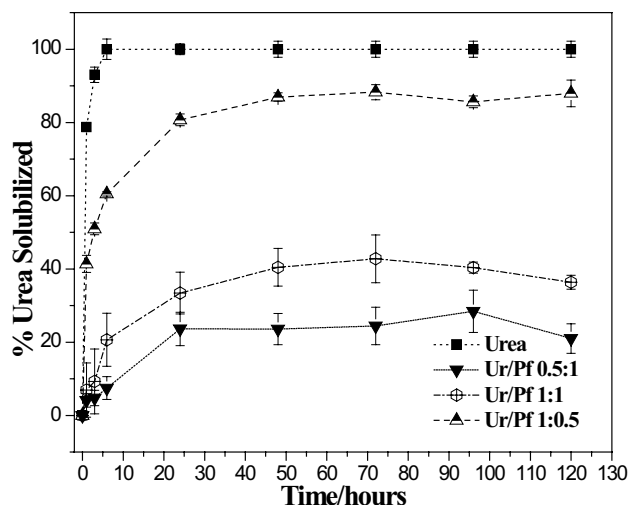


Fig. 6 Kinetics of urea release at $25\text{ }^\circ\text{C}$ in an aqueous medium (neutral pH) for commercial urea and Ur/Pf polymers

for Ur/Pf 1:1 and 0.5:1 were observed, respectively, at the end of 50 h (equilibrium time). This value is almost constant until the end of the experiment, suggesting that the maximum solubilization degree was attained. Altogether, this full immersion test is very aggressive and may not correspond to real conditions in the field, where the moisture level is limited by the soil uptake capacity.

Therefore, in order to analyze the release of nitrogen for the prepared materials in near-real conditions, incubation experiments were performed, and the influence of soil moisture and temperature on the volatilization of NH_3 and formation of NH_4^+ and NO_3^- were analyzed—as seen in Figs. 7, 8 and Table 4, respectively. The samples behavior was clearly influenced by the polymerization extent. Figure 7 shows the N recovery as NH_3 volatilized during aerobic incubation of Ur or polymers (Ur/Pf) applied in both type soils studied. The rapid urea release from the Ur treatment demonstrated the high NH_3 volatilization exceeded 60%, an amount poorly affected by the soil type (Red–Yellow or Red Oxisol). However, the hydrolysis of urea was faster in the Red–Yellow than Red, which can be observed by the over 50% ammonia volatilization until the first week for the Red–Yellow soil, while Red soil attained this level only at the third week. This result can be attributed the much higher urease activity and higher sand content of the Red–Yellow soil, as reported in Table 2, which intensifies the NH_3 volatilization trend. The high NH_3 losses from urea in the incubation experiment can be attributed to low CEC of both soils (Table 2) agreeing with Guimarães et al. [39].

The polymerization of urea with paraformaldehyde provided control of urea release, even in the partially polymerized sample (Ur/Pf 1:0.5) in both soils and inhibited the N losses (Fig. 7). This sample was characterized by

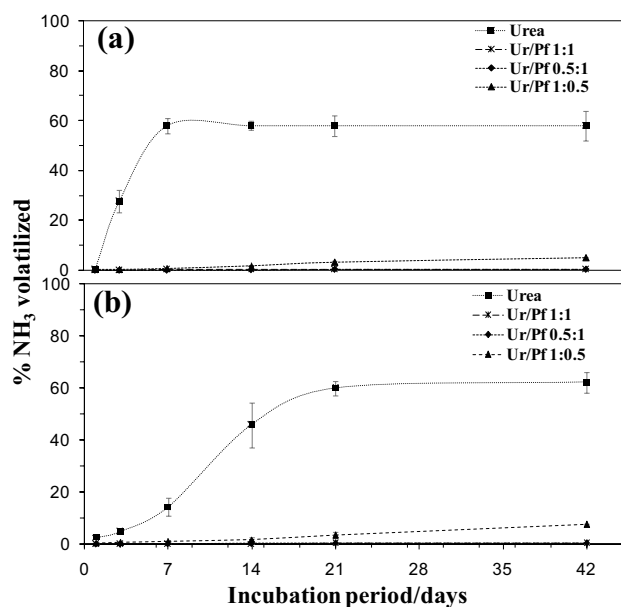


Fig. 7 Fertilizer N recovery as NH_3 volatilized during the aerobic incubation of urea (Ur), or polymers (Ur/Pf) applied to the **a** Red–Yellow Oxisol and **b** Red Oxisol. Data are shown as a mean of triplicate incubations with bars to indicate the standard error of the mean

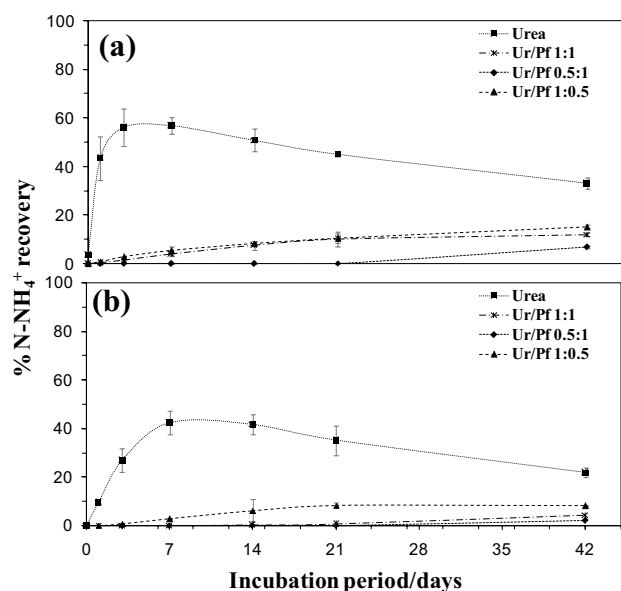


Fig. 8 Fertilizer N recovery as ammonium (NH_4^+) during the aerobic incubation of urea, or polymers (Ur/Pf) applied to the **a** Red–Yellow Oxisol and **b** Red Oxisol. Data are shown as an average of triplicate incubations with bars to indicate the standard error of the mean

a reduced polymerization degree evidenced by structural analysis (Table 3) which intensified the release of urea during the incubation period. Before urea hydrolysis, the breaking of the fragment structure and release of the urea molecule into the soil is necessary. This breaking can be

attributed to the microbial activity in soil that was faster for the treatment with low rate paraformaldehyde. It is important to notice that, even with this sample presenting a possible significant amount of low molecular weight polymers, by the synthesis conditions, these soluble molecules were also effective to reduce the total NH_3 volatilization.

Figure 8 shows recovery of exchangeable NH_4^+ during the incubation period in the Oxisols. The NH_4^+ content reflects production through urea hydrolysis, primarily consumption via NH_3 volatilization and low effect of nitrification. For both soils, the unamended urea shows a fast NH_4^+ content increase until the first week after application in the soil, however, it is followed by a decrease provided by the loss of N from ammonia volatilization. The polymers provide a more constant and homogeneous NH_4^+ release during the incubation period. Unfortunately, the content of NH_4^+ from Ur/Pf composites was low during the 6-week study attributed to high control urea release, which is consistent with the evidence of the increase rate of paraformaldehyde in the treatments. The smallest polymerization of Ur/Pf 1:1 and Ur/Pf 1:0.5 provided higher of NH_4^+ release than Ur/Pf 0.5:1 during incubation in Red–Yellow and more consistent for Ur/Pf 1:0.5 than other treatments in Red Oxisol. No definite explanation can be offered for low nitrification, which remained lower than 3.5% during the incubation period for both soils.

Table 4 compares the fertilizer N recovery as total volatilized NH_3 , and total exchangeable NH_4^+ and NO_3^- after aerobic incubation intervals of urea and composites (Ur/Pf) in two Oxisols. In both soils, the total N losses from urea alone showed similar behavior exceeding 60%. In contrast, the Ur/Pf 1:0.5 treatment did not exceed 8%, while the treatment with the highest polymerization degree showed insignificant N losses. This advantage evidences the efficiency of the paraformaldehyde to control urea release and N losses.

Similarly, the lower total NH_4^+ content of composites compared to the Ur treatment can be attributed to the more gradual release of urea. Therefore, the increase of the polymerization paraformaldehyde percentage decreases NH_4^+ content in the soil. However, the Ur/Pf polymers present high urea content without release to the soil after 6 weeks of incubation, which could be released in the longer period.

The total N recovery as NH_3 , NH_4^+ , and NO_3^- from unamended urea was 96% for Red–Yellow and 92% for Red Oxisol (Table 4). In contrast, the total N recovery of composites does not exceed 24%, which demonstrates that these compounds have more than 75% N to be released after 42 days. The N recovery as exchangeable NO_3^- did not show differences between the treatments, with values not exceeding 3.5% for Red–Yellow and 2.8 for Red Oxisol.

Table 3 ^{13}C NMR solid chemical shifts of some of the structural fragments that appear in the Ur/Pf resins showed in Fig. 4

Structural fragment	Name of group/ Typical signal (ppm)	Chemical shift/ppm		
		Samples (Ur/Pf)		
		1:0.5	1:1	0.5:1
	Methylenes 47-48	46.9	47.02	47.0
	53-54	-	-	54.0
	60-61	61.0	60.82	60.1
	Hydroxymethyls 65-66	-	65.12	65.8
	71-72	-	-	71.0
	Dimethylene ethers 74.4-75.5	-	76.0	-
$\text{>N}-\overset{\text{O}}{\parallel}{\text{C}}-\text{N}<$	Carbonyl regions			
Free urea	162	160.8	160.3	159.8
Monosubstituted urea	160-161			
Disubstituted urea	159-160			
Trisubstituted urea	158.5-159.0			

Table 4 Fertilizer N recovery as NH_3 volatilized and exchangeable NH_4^+ and NO_3^- after aerobic incubation of Red–Yellow or Red Oxisol

Treatment	Total NH_3 (%)	Total NH_4^+ (%)	Total NO_3^- (%)
Red–Yellow			
Ur	60.4 a ¹	33.2 a	3.24 a
Ur/Pf 1:0.5	5.02 b	15.5 b	3.51 a
Ur/Pf 1:1	0.35 c	12.2 c	3.38 a
Ur/Pf 0.5:1	0.35 c	7.1 d	2.84 a
Red			
Ur	62.16 a	27.26 a	2.75 a
Ur/Pf 1:0.5	7.51 b	8.47 b	1.86 a
Ur/Pf 1:1	0.28 c	4.33 c	2.80 a
Ur/Pf 0.5:1	0.28 c	2.06 c	2.30 a

¹Mean values reported from triplicate incubations. Values within a column followed by the same letter do not differ significantly by the Duncan test at $p < 0.05$

Conclusion

The results showed a simple method, based on mixing–melt of urea with different amounts of paraformaldehyde, that was effective to produce N controlled release materials. The composition plays a key role in the release profiles since the polymerization extent was shown as the mechanism needed to delay N solubilization. This was only possible by controlling the in-situ production of formaldehyde through the degradation of a solid precursor, paraformaldehyde, in processing conditions comparable to the expected for melt extrusion. It is worthy to mention that, in this strategy, the conventional setup for polymer extrusion processing may be easily adapted to produce this kind of fertilizer, which is an important technological advance compared to the conventional fertilizing products. This also influences on the actual chain length, i.e., the partial polymerization was shown as an effective strategy to produce oligomers and low-molecular-weight polymers, which will interact faster to the soil biota—releasing the nutrient. Also, the soil

profile, analyzed in two Oxisols, was seen as an important factor for release: soils with higher urease activity induced higher polymer solubility, however at low levels—indicating that these materials can avoid volatilization effects, even in the low-polymerized materials (with higher free urea contents). Finally, considering that the polymers are expected to continue their degradation behavior, the residual N in the structure is maintained for further use in the soil, as desired in many agricultural practices.

Acknowledgements This work was supported by FAPESP (Sao Paulo Research Foundation, Grant No. 2013/11821-5 and 2016/09343-6), CNPq, and CAPES. We also acknowledge the Agronano Network (Embrapa Research Network) and National Nanotechnology Laboratory for Agribusiness (LNNA) for the institutional support and facilities.

References

- Lara Cabezas WAR, Korndorfer GH, Motta A (1997) Volatilização de N-NH₃ na cultura de milho: II. avaliação de fontes sólidas e fluidas em sistema de plantio direto e convencional. *Rev Bras Ciênc Solo* 21:481–487
- Melo HB Jr, Duarte IN, Silva AA, Lana RMQ (2011) Uso de fontes revestidas com polímeros de liberação gradual e ureia convencional. *Enc Bio* 6:1–12
- Suherman I, Anggoro DD (2011) Producing slow release rate urea by coating with starch/acrylic acid in fluid bed spraying. *Int J Eng Technol* 11:62–66
- Zarei A, Ghaffarian V (2013) Preparation and characterization of biodegradable cellulose acetate-starch membrane. *Polym Plast Technol* 52:387–392
- Vieira BARM., Teixeira MM (2004) Adubação de liberação controlada chega como solução. *Revista Campo e Negócios, Uberlândia*
- Yamamoto CF, Pereira EI, Mattoso LHC, Matsunaka T, Ribeiro C (2016) Slow release fertilizers based on urea/urea-formaldehyde polymer nanocomposites. *Chem Eng J* 287:390–397
- Trenkel ME (2010) Slow- and controlled-release and stabilized fertilizers: an option for enhancing nutrient use efficiency in agriculture IFA. International Fertilizer Industry Association, Paris
- Dave AM, Mehta MH, Aminabhavi TM, Kulkarni AR, Soppimath KS (1999) A review on controlled release of nitrogen fertilizers through polymeric membrane devices. *Polym Plast Technol Eng* 38:675–711
- Neyman GB, Derr EA (2002) Homogeneous granules of slow-release fertilizer and method of making the same. Patent US 011087:A1 31 Jan 2002
- Jahns T, Ewen H, Kaltwasser H (2003) Biodegradability of urea-aldehyde condensation products. *J Polym Environ* 11:155–159
- Gabrielson KD, Epling ML (2011) Reaction products and methods for making and using the same cross-references to related applications. Patent WO 201113793-A1, 03 Nov 2011
- Sutton AR, Case M, Healey TJ (2010) Urea formaldehyde polymer additive for odor control of unmanipulated manure. Patent WO 2010093462-A1:19 Aug 2010
- Phillips JC (2008) Extended-release urea-based granular fertilizer. Patent US 2008141747-A1, 19 Jun 2008
- Phillips JC, Wertz SL, Cochran AK, Gabrielson KD, Phillips YAC (2006) High nitrogen liquid fertilizer. Patent US 2006196241-A1, 07 Sept 2006
- Phillips JC, Pace CB, Holt TG, Cochran KD (2005) Extended-release nitrogen-containing granular fertilizer. Patent US 2005144997-A1:7 Jul 2005
- Kiernan JA (2000) Formaldehyde, formalin, paraformaldehyde and glutaraldehyde: what they are and what they do. *Microsc Today* 1:8–12
- Tomaszewwska M, Jarosiewicz A (2002) Use of polysulfone in controlled-release NPK fertilizer formulations. *J Agric Food Chem* 50:4634–4639
- With K, Petersen TD, Petersen B (1961) Simple spectrophotometric method for the determination of urea in blood and urine. *J Clin Pathol* 14:202–204
- Nelson DW, Sommers LE (1996) Methods for the determination of total organic carbon (TOC) in soils and sediments. In: Sparks DL, Page AL, Helmke PA, Loeppert RH, Soltanpour PN, Tabatabai MA, Johnston CT, Sumner ME (eds) *Methods of soil analysis, Part 3*. SSSA Books Series. SSSA and ASA, Madison, pp 961–1010
- Empresa Brasileira de Pesquisa Agropecuária (1979) *Manual de métodos de análise de solo*. Embrapa Solos, Rio de Janeiro
- Kilmer VJ, Alexander LT (1949) Method of making mechanical analyses of soils. *Soil Sci* 68:15–24
- Tabatabai MA, Bremner JM (1972) Assay of urease activity in soils. *Soil Biol Biochem* 4:479–487
- Kempers AJ, Zweers A (1986) Ammonium determination in soil extracts by the salicylate method. *Commun Soil Sci Plant Anal* 17:715–723
- Yang JE, Kim JJ, Skogley EO, Schaff BE (1998) A simple spectrophotometric determination of nitrate in water, resin, and soil extracts. *Soil Sci Soc Am J* 62:1108–1115
- Roumeli E, Papadopoulou E, Pavlidou E, Vourlias G, Bikiaris D, Paraskevopoulos KM, Chrissafis K (2012) Synthesis, characterization and thermal analysis of urea-formaldehyde/nanoSiO₂ resin. *Thermochim Acta* 527:33–39
- Lundström A, Andersson B, Olsson L (2009) Urea thermolysis studied under flow reactor conditions using DSC and FT-IR. *Chem Eng J* 150:544–550
- Liu Y, Tian Y, Zhao G, Sun Y, Zhu F, Cao Y (2008) Synthesis of urea-formaldehyde resin by melt condensation polymerization. *J Polym Res* 15:501–505
- Christjanson P, Siimer K, Pehk T, Lasbn I (2002) Synthesis of urea-formaldehyde resin by melt condensation polymerization. *Holz Roh Werkst* 60:379–384
- Taylor R, F'ragnell RJ, McLaren JV, Snape CE (1982) Evaluation of NMR spectroscopy for the quantitative characterization of urea-formaldehyde resins. *Talanta* 29:489–494
- He G, Yan N (2004) ¹³C NMR study on structure, composition and curing behavior of phenol-urea-formaldehyde resole resins. *Polymer* 45:6813–6822
- Hoong YB, Pizzi A, Chuah LA, Harun J (2015) Phenol-urea-formaldehyde resin co-polymer synthesis and its influence on Elaeis palm trunk plywood mechanical performance evaluated by ¹³C NMR and MALDI-TOF mass spectrometry. *Int J Adhes Adhes* 63:117–123
- Fan D, Chang J, Li J, Mao A, Zhang L (2009) ¹³C-NMR study on the structure of phenol-urea formaldehyde resins prepared by methylolureas and phenol. *J Appl Polym Sci* 112:2195–2202
- Tomita B, Ohyama M, Hse C-Y (1994) Synthesis of phenol-urea-formaldehyde co-condensed resins from UF-concentrate and phenol. *Holzfoncbung* 48(6):522–526
- Edoga MO (2006) Comparative study of synthesis procedures for urea-formaldehyde resins Part I. *Leonardo Electron J Pract Tehnol* 9:63–80
- Samarzija-Jovanovic S, Jovanovic V, Konstantinovic S, Markovic G, Marinovic-Cincovic M (2011) Thermal behavior of modified urea-formaldehyde resins. *J Therm Anal Calorim* 104:1159–1166

36. Jada SS (1988) The structure of urea–formaldehyde resins. *J Appl Polym Sci* 35:1573–1592
37. Mattos EC, Viganó I, Dutra RCL, Diniz MF, Iha K (2002) Aplicação de metodologias FTIR de transmissão e fotoacústica à caracterização de materiais altamente energéticos: parte II. *Quim Nova* 25(5):722–728
38. Zhong R, Gu J, Gao Z, Tu D, Hu C (2017) Impacts of urea-formaldehyde resin residue on recycling and reconstitution of wood-based panels. *Int J Adhes Adhes* 78:60–66
39. Guimarães GGF, Mulvaney RL, Khan SA, Cantarutti RB, Silva AM (2016) Comparison of urease inhibitor N-(n-butyl) thiophosphorictriamide and oxidized charcoal for conserving urea-N in soil. *J Plant Nutr Soil Sci* 179:520–528