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Cassava starch-graft-poly(acrylonitrile)-coated urea fertilizer with sustained release and water retention properties

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Abstract

Cassava starch-graft-poly(acrylonitrile) samples were synthesized by a free radical-initiated polymerization reaction, and urea fertilizer was coated with these grafted starches to obtain the dual benefit of sustained release and water retention properties. A response surface design was used to optimize the synthetic conditions of starch-graft-copolymers to maximize the slow nutrient release and water absorbency. The FT-IR analysis confirmed the grafting reaction, and scanning electron micrographs revealed the ultrastructure of polymer coating. The release of nitrogen in soil from coated urea was more sustained than that from uncoated urea and it varied with grafting level of the polymer. The uncoated urea showed almost complete release of nitrogen by 1 month, whereas %N release was in the range of 69.8%–78.3% from the grafted starch-coated urea even after 108 days of incubation. The water retention capacity of the coated urea ranged from 74.2% to 426.6% and it decreased with increase in % grafting of the coating material.

KEYWORDS
cassava starch, controlled release urea, grafted starch, soil incubation, water absorbency

1 | INTRODUCTION

The fast-growing population all over the world and the consequent increase in the demand for food emphasize the need for an increased agricultural production from the existing land and other resources. Even though over-exploitation of natural resources such as water and excessive use of fertilizers and pesticides helped to increase productivity, continuous practice of this resulted in impairment of the productive capacity of the arable land, depletion of water resources, and pollution with hazardous pesticides and chemical fertilizers. As the available land for agricultural is limited, there is an urgent need for switching over to more efficient and judicious use of the existing resources and agricultural inputs.

In agriculture, loss of nutrient elements is a large problem which causes insufficient plant nutrients, increase in process cost, and pollution of the environment. Controlled release systems help to release the fertilizer nutrients at a slower rate.[1] Controlled release fertilizers (CRFs) help to increase the efficiency of nutrient uptake by plants, reduce the risk of overdosing, and prevent leaching of fertilizers from the soil.[2–4] CRFs based on various materials have been reported. Polymer coating of fertilizer granules is the most commonly applied controlled release mechanism, and fertilizer is released due to biodegradation of the polymer. Polymer hydrogels, which can swell without dissolving in water and retain a significant amount of water within their network structures, are potential materials for the development of CRFs.[5,6] Starch is a natural biopolymer and is widely used for hydrogel preparation either in its modified form or as composites/blends. Han et al.[7] developed slow release fertilizer by incorporating urea in starch/polyvinyl alcohol/acacia-based films. Controlled release nitrogen, phosphorous, and potassium compound fertilizer with excellent water retention function was prepared by

Liang et al.[8] Fluid bed spraying technology has been utilized by Suherman and Anggoro[9] in developing urea coated with starch/acrylic acid and polyethylene glycol. Talaat et al.[10] reported the experimental investigations for developing a multicomponent fertilizing hydrogel based on starch, urea, zinc, potassium, and phosphorous and using these hydrogels, they could get a significant increase in wheat grain and faba bean seed yields. To improve the utilization of phosphate rock fertilizer and to integrate water retention and controlled release properties, an agricultural superabsorbent polymer based on sulfonated corn starch/poly(acrylic acid) embedding phosphate rock has been prepared and tested.[11] Jamnongkan and Kaewpirom[12] prepared a controlled release phosphorus fertilizer based on chitosan hydrogel, whereas Abed et al.[13] has reported hydroxyethyl cellulose cross-linked with borax as a matrix for the slow delivery of urea and liquid NP fertilizers. Davidson et al.[14] reported the development of a controlled root targeted delivery fertilizer using ionically cross-linked carboxymethyl cellulose hydrogel matrix with increased fertilizer use efficiency. Encapsulation of fertilizers in polymeric nanoparticles was reported.[15–17] Poly(acrylonitrile) has been used as a coating for soluble NPK granular fertilizer in CRF formulations, and the effect of coating structure on the release rate was investigated.[18]

Along with nutrients, water also is an essential resource for proper plant growth. In the present scenario of depleting water resources and increasing demand for water in agriculture, the means for water conservation deserve special attention. In this regard, hydrogels have an important role to play. To improve the utilization of fertilizer and water resource at the same time, a new type chitosan-coated NP&K compound fertilizer with controlled release and water retention properties was prepared, which had an inner coating of chitosan and an outer coating of polyacrylic acid-*co*-acrylamide superabsorbent polymer.[19] A slow release nitrogen fertilizer with high water absorbency was prepared based on poly(acrylic acid-acrylic amide)/Na-Bentonite by Qin et al.[20]

This study was an attempt to develop a novel urea fertilizer with slow release properties and water absorbency based on cassava starch-graft-poly(acrylonitrile). The study was aimed at optimization of the synthetic conditions of the polymer to get best slow release properties and water absorbency, characterization of the developed products, and evaluation of nutrient release behavior.

2 | MATERIALS AND METHODS

2.1 | Materials

Cassava starch was extracted from freshly harvested tubers of cassava obtained from the farm of ICAR-Central Tuber Crops Research Institute, Thiruvananthapuram, Kerala, India. The moisture content of the starch was 12.5%, and the amylose content was 20.4%. Acrylonitrile and N,N′-Methylenebis(acrylamide) were purchased from Aldrich (St. Louis, USA) and were used without further purification. Ceric ammonium nitrate (22,249–100 g, ≥98.5%) was procured from Sigma-Aldrich (St. Louis, USA). All the other chemicals used were of analytical grade.

2.2 | Synthesis of cassava starch-graft-poly(acrylonitrile)

The graft copolymerization was carried out by a free radical-initiated polymerization reaction of the pregelatinized cassava starch with acrylonitrile (AN). Ceric ammonium nitrate (CAN) and N,N′-methylenebis(acrylamide) (MBA) were used as the free radical initiator and the cross-linking agent, respectively. A response surface Box–Behnken design was used for optimizing the reaction conditions. The variables used were as follows: weight of acrylonitrile (0.188, 0.377, 0.565 mol/10 g starch in 200 ml water), weight of CAN (0.007, 0.009, 0.011 mol/L), and weight of N,N′-methylenebis(acrylamide) (0.002, 0.004, 0.006 mol/L). Starch (10 g) was dispersed in 200 ml of distilled water with constant stirring and gelatinized by keeping in a water bath maintained at 95°C. It was then cooled and placed at 45°C in a constant temperature water bath, and nitrogen gas was purged through the solution. Ceric ammonium nitrate was then added and stirred, which was followed by addition of the required quantities of acrylonitrile and the cross-linker. The reaction mixture was stirred for 2 hr under nitrogen atmosphere. The reaction was terminated by pouring the reaction mixture into methanol to precipitate the product. The residue was then dried, powdered in a pulverizer mill, and then weighed.

2.3 | Percentage grafting and grafting efficiency

The percentage grafting and grafting efficiency were calculated as follows: [21]

$$\% \text{ Grafting} = [(W_1 - W_0)/W_0] \times 100$$

$$\text{Grafting Efficiency } (\%) = [(W_1 - W_0)/W_2] \times 100$$

where W_0, W_1, and W_2 are the weights of the original starch, starch-graft-copolymer, and the monomer used, respectively.

2.4 | Nitrogen content

The nitrogen content in the grafted starches was determined according to the method of Vogel.[22]

2.5 | FT-IR analysis

Infrared spectra of the native starch and graft copolymers were recorded on a Thermo Nicolet, Avatar 370 (Thermo Nicolet Corporation, Madison WI, 53711) in the spectral range of 400–4,000 cm^{-1} using KBr background spectrum.

2.6 | Scanning electron microscopy

The ultrastructure of the native starch as well as the graft copolymers was studied using a scanning electron microscope (JEOL/EO, Model JSM-6390, JEOL, Tokyo, Japan) after coating the samples with gold films.

2.7 | X-ray diffraction analysis

A Bruker X-Ray diffractometer (Model D8 Advance, Bruker AXS Inc., Madison, WI, USA) with Cu (K_α radiation $\lambda = 1.5406$ A°) source was used for recording the powder X-ray diffraction patterns of the native cassava starch and the graft copolymers.

2.8 | Thermal analysis

Thermogravimetric analysis of the polymers was carried out on a TG/DTA analyzer (Diamond, Perkin Elmer Inc., Shelton, CT, USA). Heating was performed from 40 to 990°C at 20°C/min in nitrogen atmosphere.

2.9 | Preparation of coated fertilizer

A coating machine was used for coating of fertilizers with the grafted starch. Fertilizer was placed in the rotating vessel of the granulator. Then, a small amount of native starch was added as a binding material and coated as a thin layer with spraying of water, in between. Then, starch-graft-copolymer was added as the coating layer, and coating was continued till small granules were formed. The granules were then dried at 50°C in an air oven. A total of 15 samples of coated fertilizers were prepared using different starch-graft-copolymers and they were labeled as S1 to S15.

2.10 | Characterization of the coated fertilizer

The diameter of the coated fertilizer granules (30–40 granules per each lot) was measured using a Vernier Calipers, and the mean value was calculated.

2.11 | Percentage coating

The percentage coating (% shell material) of the samples was determined as follows: 500 mg of the coated fertilizer was immersed in 100 ml of deionized water. After vigorous shaking, the coating was liberated, and subsequently, it was obtained by filtration and drying. The coating percentage was calculated from the following equation:

$$\% \text{ Coating} = (M_i - M_o)/M \times 100$$

where M_i, M_o, and M were the weights of filter paper along with sample, empty filter paper, and the sample, respectively.

2.12 | Water absorbency

The water absorbency of the coated urea samples was determined according to the method reported by Wu and Liu.[19] Briefly, one gram of coated urea was immersed in 100 ml of tap water and allowed to soak at room temperature for 90 min. The swollen fertilizer was filtered through an 80-mesh sieve to remove the nonabsorbed water and weighed. Water absorbency per gram of the dry fertilizer was calculated using the following equation:

$$\text{Water absorbency} = \frac{M - M_o}{M_o}$$

where M and M_o are the weights of the swollen and dry fertilizer, respectively.

2.13 | Release behavior of coated urea in soil

To study the release behavior of coated urea in soil, a method described by Wu and Liu[19] was used with slight modifications. The soil used in the experiment was laterite sandy clay loam soil collected from 20 to 25 cm depth from the ICAR-Central Tuber Crops Research Institute farm. The soil was dried, ground, and passed through a 2-mm sieve. Two hundred grams of portions of the soil was taken in plastic beakers. Coated urea (0.5 g) was well mixed with the soil, properly covered, and incubated at room temperature. Throughout the experiment, the soil was maintained at a moisture content of 30 wt%. After 7, 14, 21, 28, 43, 72, and 108 days of incubation, soil was taken from the beakers, air-dried, and the released nitrogen was estimated by the Kjeldahl method. [23]

3 | RESULTS AND DISCUSSION

3.1 | Grafting parameters of cassava starch-g-poly(AN)

The response surface experimental design used for the synthesis of cassava starch-graft-copolymers and the grafting parameters of various samples are presented in Table 1. The % grafting was highest for the sample S4 (221%) and lowest for S8 (39.6%). The grafting efficiency ranged from 38.8%

TABLE 1 Synthetic conditions, grafting parameters and water and saline retention of cassava starch-g-poly(acrylonitrile)

Sample	AN[b]	CAN (mol/L)	MBA (mol/L)	%G	%GE	N (%)[a]	Water retention (g/g)[a]	Saline retention (g/g)[a]
S1	0.188	0.007	0.004	46.8	46.8	8.9	8.61	8.9
S2	0.188	0.011	0.004	44.9	44.9	8.4	8.96	8.12
S3	0.565	0.007	0.004	181.3	60.4	17.7	2.73	2.29
S4	0.565	0.011	0.004	221.0	73. 7	18.6	2.01	2.13
S5	0.377	0.007	0.002	121.6	60.8	15.1	3.52	4.16
S6	0.377	0.007	0.006	108.9	54.4	13.5	4.79	4.92
S7	0.377	0.011	0.002	136.4	68.2	16.7	2.92	2.76
S8	0.377	0.011	0.006	39.6	39.6	7.8	9.68	9.12
S9	0.188	0.009	0.002	59.0	59.0	10.8	6.92	7.97
S10	0.565	0.009	0.002	160.0	53.3	17.1	3.17	2.75
S11	0.188	0.009	0.006	100.6	40.6	12.8	5.11	5.22
S12	0.565	0.009	0.006	116.6	38.8	14.4	4.23	4.13
S13	0.377	0.009	0.004	127.9	63.9	15.9	3.31	2.16
S14	0.377	0.009	0.004	129.0	64.5	16.2	3.19	2.40
S15	0.377	0.009	0.004	129.8	64.9	16.4	3.19	2.72

[a]Values are the mean of three replications

[b]mol/10 g starch in 200 ml water

to 73.7%. Analysis of the data showed a positive linear relation between % grafting and concentration of the monomer used for the preparation of the graft copolymer. However, grafting efficiency was found to be higher at lower concentrations of the cross-linking agent, MBA. The other grafting parameters had no significant effect on % grafting and grafting efficiency within the levels used. The nitrogen content in the grafted starches (7.8%–18.6%) increased with increase in concentration of the monomer used. The linear relationship between grafting parameters and concentration of acrylonitrile/MBA is given by the following predictive regression equations. R^2 indicates the coefficient of determination.

$$\text{Percentage grafting (\%G)} = 8.14 + (283.48 \times \text{Conc. of acrylonitrile}) \quad (R^2 = 80.72\%)$$

$$\text{Grafting efficiency (\%GE)} = 72.54 - 4238.8 \times \text{Conc. of MBA} \quad (R^2 = 79.55\%)$$

The nitrogen content in the grafted starches also showed a similar trend as in the case of %G (Table 1). It was in the range of 7.8%–18.6% with S4 and S8 showing the highest and lowest N contents, respectively. There was a positive correlation between %G and nitrogen content, and this could be due to the presence of more number of nitrile groups in the grafted starches at higher grafting levels. The concentration of acrylonitrile used for the synthesis of the graft copolymer was found to have a significant positive effect on nitrogen content. Similar result was reported earlier also.[24]

3.2 | FT-IR analysis

The FT-IR spectra of native cassava starch and that of the grafted starches confirmed the grafting reaction of starch with poly(acrylonitrile) (Figure 1). The major IR absorptions of native cassava starch were in the regions of 3,382 cm^{-1}(O–H stretching), 2930.3 cm^{-1} (C–H stretching), and 1650.7 cm^{-1} (C=O stretching). The characteristic triplet band was observed at 1,158, 1084.7, and 1004.7 cm^{-1} (C–O–C stretching) (Figure 1a). A strong absorption peak at 2,240 cm^{-1} in the case of starch-g-poly(acrylonitrile) samples (S4 and S8) was responsible for the nitrile group (-C≡N), which confirmed the grafting reaction (Figure 1b and c). Other major absorptions of starch were also present in the FT-IR spectra of the grafted starches but with different intensities.

3.3 | Scanning electron microscopy

The scanning electron micrograph of the native cassava starch showed its granular nature (Figure 2a). The starch granules appeared spherical with a flat surface on one side containing one or more pits, which is the typical granular morphology of cassava starch.[24] However, starch-g-poly(AN) showed no granular appearance (Figure 2b and c). The surface was nonuniform and nonplanar with gelatinized mass-like appearance. The pregelatinization of starch and the subsequent grafting reaction might be responsible for the observed differences in the morphological structure. Similar observations of loss of uniformity and planarity were reported earlier with cassava starch-graft-poly(AN)[24] as well as cassava and potato starches grafted

with acrylamide and polyethylene.[25–27] The change in morphological structure confirmed the grafting reaction of starch.

3.4 | X-ray diffraction analysis

Native cassava starch exhibited a typical A-type X-ray diffraction pattern with major peaks at diffraction angles, $2\theta = 14.982°$ ($d = 5.9085$), $16.943°$ (doublet) ($d = 5.2288$), $17.742°$ ($d = 4.9950$), $22.874°$ ($d = 3.8864$), and $19.711°$ ($d = 4.5002$) (Figure 4). In the case of starch-graft-poly(acrylonitrile) samples, the pattern was different from that of native starch. Only one major peak was observed for all the grafted starches at around $17.131°$ ($d = 5.17183$), which accounted for about 99.9% relative intensity, and this structure resembled B-type XRD crystalline pattern. The XRD patterns of representative samples, S4 and S9, are shown in Figure 3. This result was consistent with earlier reports by Jyothi et al.[24] Aged thermoplastic maize starch–zein blends were reported to produce similar types of XRD patterns due to the
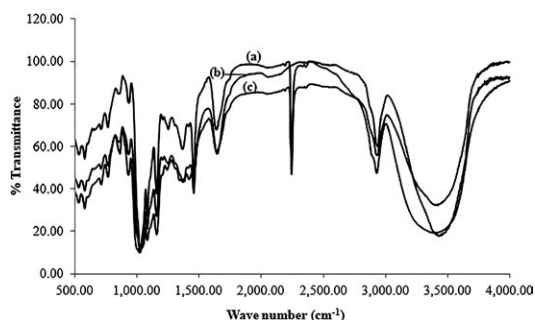
**FIGURE 1** FT-IR spectra of (a) grafted starch S4, (b) native cassava starch, and (c) grafted starch S8

crystallization of the short outer chains of amylopectin.[28] In the present study also, the pregelatinization of cassava starch prior to grafting reaction and subsequent cooling might have resulted in the B-type crystalline structure. There was a significant reduction in the percentage crystallinity of the starch as a result of grafting reaction. The percentage relative crystallinity was 42.1 for the native cassava starch, whereas it was in the range of 23.3 to 35.4 for the various grafted starches.

3.5 | Thermal properties

The thermograms of native and grafted starches are shown in Figure 4. The native cassava starch showed a three-step thermogram, and the major weight loss was observed in the temperature range of 277–357°C in the second step. As the initial degradation temperature of both the native starch and grafted starches was almost similar, there was no significant change in the thermal stability. The weight retention of the grafted starches at the end of the heating cycle was about 25%–30%, and this could be due to the increased nitrogen content in the samples. Increased weight retention and thermal stability of starch-g-poly(AN) in comparison with native starch have been reported earlier also.[24,29]

3.6 | Water and saline retention

The water retention capacity of the grafted starches ranged from 2.01 to 9.68 g/g dry starch, and the saline water retention was in the range of 2.13–9.12 g/g (Table 1). The maximum water retention as well as saline water retention was obtained for urea coated with the grafted starch, S8, with lowest %G, which was synthesized under the following reaction
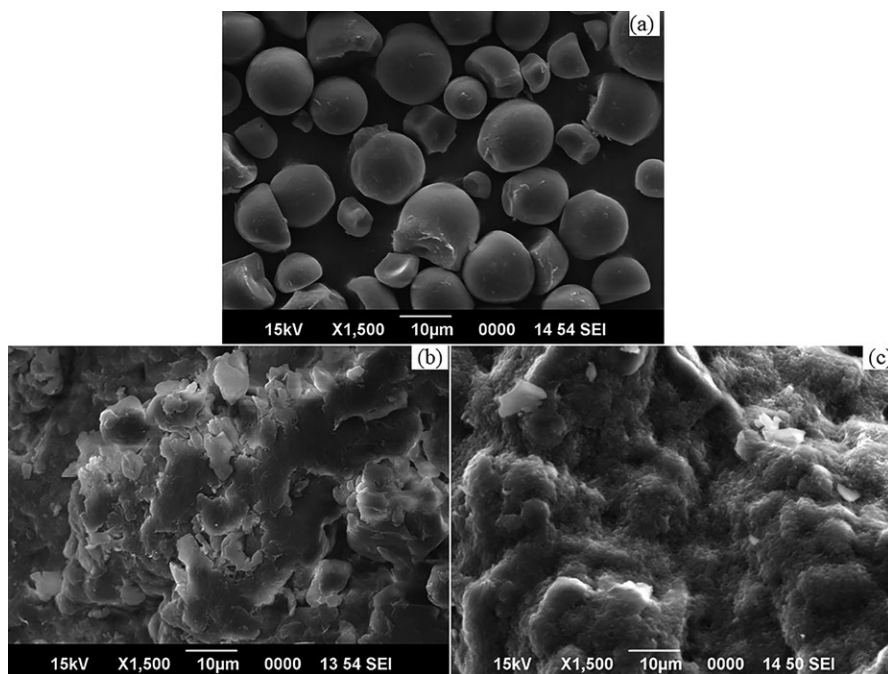
FIGURE 2 Scanning electron micrographs of (a) native cassava starch, (b) grafted starch S4, and (c) grafted starch S8
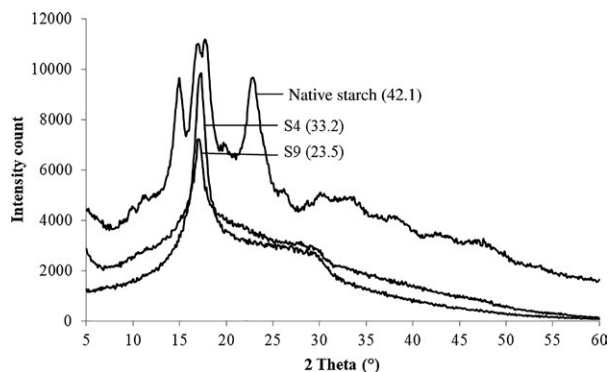
FIGURE 3 X-ray diffraction patterns of native cassava starch and starch-graft-poly(acrylonitrile) *The % relative crystallinity is shown in brackets
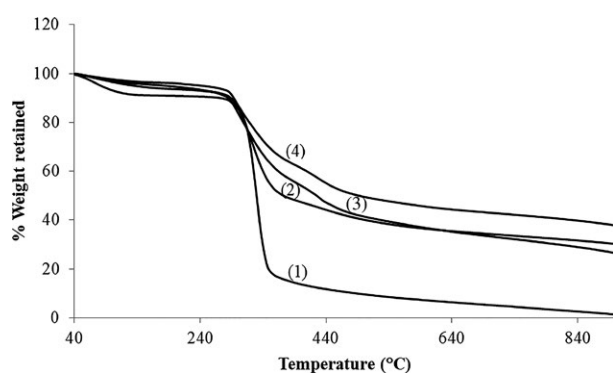
FIGURE 4 Thermogravimetric curves of (1) native cassava starch, (2) grafted starch S9, (3) grafted starch S3, and (4) grafted starch S4

conditions: concentration of acrylonitrile = 0.377 mol/10 g starch in 200 ml water, CAN = 0.011 mol/L and MBA = 0.006 mol/L. For each grafted starch, the percentage water and saline water retentions were almost similar, that is, the water retention capacity of the grafted starches did not alter under saline conditions. This is a favorable characteristic while saline soil applications are considered. It was observed that the water retention and saline retention capacities were higher at lower grafting levels. This could be due to the presence of more hydrophobic grafts at higher grafting levels, which results in lower water absorption. Similar result was earlier reported by Jyothi et al.,[24] on the water and saline retention of cassava starch-graft-poly(acrylonitrile), and they have observed a negative correlation between percentage grafting and water retention capacity. The concentration of acrylonitrile was found to have a significant negative effect on water retention as well as saline water retention.

3.7 | Properties of urea coated with grafted starch

Urea coated with cassava starch-g-poly(AN) is shown in Figure 5. The diameter of the coated urea granules was in

FIGURE 5 Urea coated with cassava starch-g-poly(acrylonitrile)

TABLE 2 The % shell material and water absorbency of coated urea samples[a]

Urea coated with starch-g-poly(AN)	% Shell material	Water absorbency (%)
S1	33.2	271.20
S2	37.6	345.13
S3	23.7	175.70
S4	38.1	74.19
S5	30.8	377.74
S6	29.0	86.77
S7	33.3	405.62
S8	35.6	426.64
S9	35.5	167.08
S10	34.7	270.96
S11	24.5	282.71
S12	22.7	230.98
S13	28.9	107.23
S14	25.0	348.32
S15	28.0	445.32

[a]Values are the mean of three replications.

the range of 1.83–2.12 mm (data not shown). The % shell material was in the range of 22.7%–38.1%. The coated urea samples showed water retention capacities in the range of 74.2%–426.6% (Table 2). The water retention capacity was lowest for urea coated with the grafted starch, S4 (74.2%), whereas it was highest for the sample coated with S8 (426.6%). There was a decrease in water retention capacity with increase in percentage grafting of the coating material. This could be explained on the basis of increased
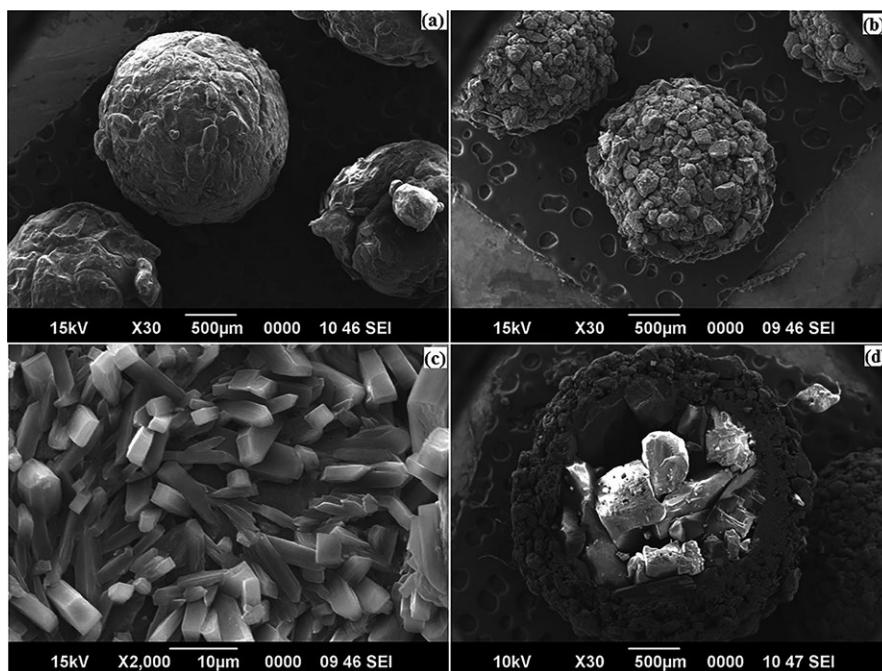
FIGURE 6 Scanning electron micrographs of (a) uncoated urea, (b) coated urea at ×30, (c) coated urea at ×2000, and (d) cross section of coated urea

hydrophobicity at higher levels of grafting due to the introduction of more number of acrylonitrile groups in the grafted starch.

3.8 | Surface morphology of coated urea

The scanning electron microscopic images revealed the change in morphology due to coating of urea (Figure 6). The particles of uncoated urea appeared as spheres. Figure 6a shows the granule morphology of urea with magnification of ×30. The coated urea particles also appeared spherical but with a highly nonuniform and uneven surface, clearly indicating a layer of polymer particles on the surface. Figure 6(c) at a higher magnification (×2,000) shows the layering of grafted starch on the surface of the urea particles. In the cross-sectional view of the coated granule, the polymer layer can be seen on the surface of urea particles (Figure 6d), which make its release slower. A phase separation was noticed in the case of coated fertilizers. In a recent study, where liquid coating was used, a more uniform, smooth, and compact surface layer of polymer was observed.[30] In the present study, the grafted starch particles in the coating layer appeared cylindrical and independent with a noncontinuous phase, which might be due to the fact that the coating was performed with grafted starch in the granular form. The polymer layer serves as a barrier to the release of urea into the environment.

3.9 | Release behavior of urea in soil

Figure 7 shows the release of N (%) from the applied fertilizers into the soil after different periods of soil incubation. About
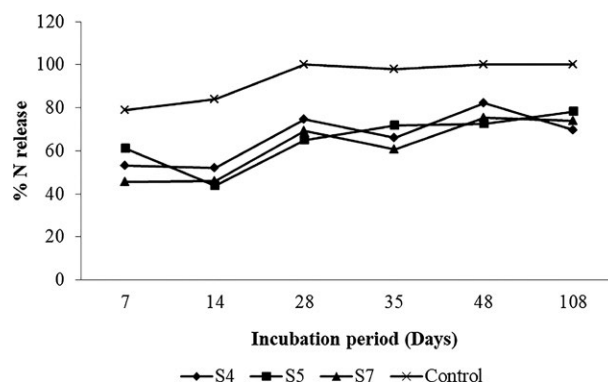
FIGURE 7 Percentage release of nitrogen from coated and uncoated urea at different periods of soil incubation

79% of nitrogen was released from the control, that is, the uncoated urea after 7 days of incubation. The coated samples showed significantly lower nitrogen release (45.5%–61%) during the same period. By 28th day of incubation, about 100% of nitrogen was released from uncoated urea. In the case of coated fertilizers, extended release of N was observed. After 108 days of incubation, %N release was in the range of 69.8%–78.3% for the coated urea samples. Wu and Liu[19] reported a release of about 79% of urea from a double-coated compound fertilizer on 30th day. Suherman and Anggoro[9] observed a similar decrease in dissolution rate of urea coated with acrylic acid polymer by fluid bed spraying. The mechanism of release of urea from the coated granules could be explained as follows. First, water present in the soil penetrates the coating and dissolves the urea in the core. In the second step, the solution of urea diffuses through the coating into the environment. In the present study, the starch-graft-poly(acrylonitrile) used

for coating imparts more hydrophobic nature to the granules and causes a lagging in the penetration of water into the core through this surface layer. This also might be a contributing to the observed sustained release property of the coated urea.

4 | CONCLUSIONS

Cassava starch-g-poly(acrylonitrile) was used for coating urea granules to obtain sustained release properties coupled with water retention capacity. The coated urea exhibited controlled release of the nutrient in soil, and the release depended on the grafting percentage of the coating material. Due to the introduction of hydrophobic acrylonitrile groups, there was a decrease in water penetration into the urea granules which reduces its dissolution and subsequent release into the soil. In spite of being an industrial starch in many Asian countries, cassava starch has not yet been utilized for this purpose. Diversification of the use of cassava starch will fuel the starch industry and ultimately benefit the cassava-cultivating farmers. In this study, along with controlled release property, water retention capacity also could be achieved through coating urea with grafted cassava starch, which will be beneficial in terms of more efficient utilization of water and fertilizer.

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