Multilayer-Coated NPK Compound Fertilizer Hydrogel with Controlled Nutrient Release and Water Absorbency

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ABSTRACT: A novel trilayered controlled-release nitrogen, phosphorous, and potassium (NPK) fertilizer hydrogel was prepared by dipping the NPK fertilizer granules sequentially in 7% w v^{-1} poly(vinyl alcohol) (PVA) and 2% w v^{-1} chitosan (CS) solutions and then cross-linking the CS layer (*cross*-CS) via glutaraldehyde vapor deposition. Different NPK fertilizer hydrogels were then synthesized by inverse suspension polymerization of the dried PVA/*cross*-CS bilayer-coated fertilizer granules in various molar ratios of acrylamide (AM) and acrylic acid (AA) monomers, and polymerization with varying molar ratios of ammonium persulfate, *N,N,N′,N′*-tetramethylethylenediamine and *N,N′*-methylenebisacrylamide (*N*-MBA). The water dissolution time of the obtained PVA/*cross*-CS/poly (AA-*co*-AM) trilayer-coated NPK fertilizer hydrogel granules was prolonged, while the water absorbency increased with increasing AA contents, and decreased with increasing *N*-MBA contents in the outer poly(AA-*co*-AM) coating. The optimal trilayer-coated NPK fertilizer hydrogel obtained released 84 ± 18, 63 ± 12, and 36 ± 15% of the N, P, and K nutrients, respectively, after a 30-day immersion in water. The release phenomena of the N, P, and K nutrients of the fertilizer hydrogel obeyed both the Korsmeyer-Peppas and Ritger-Peppas models with a pseudo-Fickian diffusion mechanism. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41249.

KEYWORDS: compound fertilizer hydrogel; controlled release; crosslinking; gels; hydrophilic polymers; kinetics; swelling

INTRODUCTION

Fertilizers and water are vital factors for producing high yield agricultural crops. Generally, fertilizers are comprised of nutrients for plants in the form of water soluble salts, where the nitrogen, phosphorous, and potassium (NPK) fertilizers are compound fertilizers composed of nitrogen (N), phosphate (P), and potassium (K) nutrients in any soluble salt form. There are many weight ratios of NPK fertilizer available in the market place, such as 10 : 10 : 10, 17 : 17 : 17, and 8 : 24 : 24. Plants cannot absorb all of the total soluble salts in the fertilizer within the very short time they are available from their initial application due to the high water solubility and fast dissolution of these salts and their subsequent leaching away from the vicinity of the plant roots. Thus, a significant proportion of the nutrients from these fertilizers are lost to the surrounding environment where they cause serious environmental pollution in addition to the economic loss to agriculture. Therefore, controlled slow-release fertilizers are one key approach for reducing the nutrient losses from applied fertilizers and the associated economic costs and environmental problems. Coated-fertilizers are obtained by coating granules of conventional fertilizers with various materials, such as wax, polymers or sulfur, which reduce their water dissolution rate.[1–5] In general, the thicker the coated layer, the longer the dissolution time of the coated fertilizer becomes.[2] Basically, the nutrient release rate depends on the kind of nutrient in the fertilizer and the medium, such as water, water saturated sand, and sand at field capacity. The release rate of the fertilizer nutrients has been ranked (fastest to slowest) as: nitrate > ammonium > potassium > phosphate.[2] The temperature and pH of the soil also affect the release behavior of fertilizer nutrients.[6]

Superabsorbent polymers (SAPs) are three-dimensional lightly cross-linked hydrophilic polymer networks with high water absorbency.[7,8] Slow release fertilizers can be achieved by coating the fertilizer granules via the *in situ* synthesis of a SAP outer layer. Slow release N-SAP fertilizers have been synthesized by many techniques, such as solution copolymerization of acrylic acid (AA) and maleic anhydride,[9] and by inverse suspension polymerization of AA in the presence of urea with cross-linked starch as the first layer, and a mixture of AA and acrylamide

(AM) monomers as the second layer, as well as with ammonia, borax,[10] and so on. A double-coated urea fertilizer has also been prepared using urea as the core material and cross-linked starch as the first coating layer, followed by a copolymer of AA and AM, poly(AA-co-AM) as the second coating layer.[11] Coating the urea fertilizer with ethyl cellulose as the inner layer and then cross-linked with poly(AA-co-AM) as the outer-coating layer was found to yield granules that were able to absorb tap water at 70 g g^{-1} and slowly release 75% of the N nutrient into the soil within 30 days.[12] Wu and Liu[3,4] prepared two types of controlled-release NPK fertilizers. In the first type, chitosan (CS) was used as the inner coating material and poly(AA-co-AM) as the outer coating for absorbing water and controlling the release of the N, P, and K nutrients, where their release into the soil obeyed a non-Fickian diffusion mechanism. For the second type, cellulose acetate was used as the inner coating instead of CS, and poly(AA-co-AM)/unexpanded vermiculite as the outer coating. These two different types of fertilizer had released less than 75 wt % of their nutrients into the soil after 30 days. Teodorescu et al.[13] prepared a slow release NPK fertilizer from liquid fertilizer and poly(AA). The degree of swelling of the obtained hydrogels depended on the overall concentration of reactants (monomers and initiator), liquid fertilizer composition, cross-linking agent, and initiator concentrations. By appropriately combining these reaction parameters, SAP hydrogels with DSs in distilled water ranging from a few hundred to 1000 g of water per gram of gel were obtained. The fertilizer-containing hydrogels displayed a slow release of their nutrients in distilled water at room temperature.

Poly(vinyl alcohol), PVA, is a synthetic polymer that is water-soluble due to its hydroxyl groups. Moreover, PVA also provides good physical and chemical properties, including its film-forming ability. Because PVA is non-toxic and environmentally friendly, it has been used in many applications, such as controlled drug delivery systems, membrane preparation, recycling of polymers, and packaging materials.[14] A starch/PVA blend film was used to coat soluble fertilizer granules to produce a biodegradable controlled-release fertilizer with good water absorption properties.[15] To date, PVA has not yet been established as a film former for fertilizers, and so the aim of this study was to use PVA as the first coating on and an NPK fertilizer and then to investigate the resultant water dissolution time of the compound fertilizer.

In addition to being biodegradable and environmentally relatively non-toxic, CS has both reactive amino and hydroxyl groups that can react with many reagents to modify or improve its properties under mild reaction conditions. Glutaraldehyde (GA) can crosslink CS (cross-CS) via a Schiff base reaction to give the link of the —C=N— bond,[16] and can also react with the hydroxyl groups (-OH) in CS and PVA allowing cross-linking between them.[17,18]

Due to the increasing prices of inorganic fertilizers and renewed pressure from environmental protection issues on soil and ecosystem damage, as well as on human health, this research prepared a novel trilayer-coated NPK fertilizer hydrogel to improve the utilization of the NPK compound fertilizer and conserve the environment. The effect of the first (PVA) and second (CS) coating layer, the subsequent GA-mediated cross-linking of the CS layer, and poly(AA-co-AM) third coating layer including the effects of varying the AA : AM molar ratios and the molar proportions of the initiators used in the synthesis of the poly(AA-co-AM), on the water absorbency of the obtained coated-NPK fertilizers was investigated. The amount of N, P, and K nutrient released and their kinetics of release over a 30-days immersion in water were investigated.

EXPERIMENTAL

Materials
The NPK fertilizer granules containing $(NH_4)_2SO_4$, P_2O_5 and KCl as the N, P, and K nutrient sources, respectively, were provided by Chia Tai (Bangkok, Thailand), while 100 and 200 kg mol^{-1} molecular weight (M_W) CS with a degree of deacetylation of 95% were purchased from Seafresh Chitosan (Lab; Bangkok, Thailand). The industrial grade PVA with a 100 kg mol^{-1} M_W, an 86–89% degree of hydrolysis and a 2400 degree of polymerization, and industrial grade AA were supplied by Thai Mitsui Specialty Chemicals (Bangkok, Thailand), while AM was provided by Siam Chemical Industry (Bangkok, Thailand). Analytical grade N, N′-methylenebisacrylamide (N-MBA) and N,N, N′,N′-tetramethylethylenediamine (TEMED) were purchased from Fluka (Buchs, Switzerland). Analytical grade ammonium persulfate (APS) was purchased from Ajax (Seven Hills, Australia). Sorbitan (z)-mono-9-octadecanoate (Span 80) was supplied by Kao Industrial (Thailand) (Bangkok, Thailand). Cyclohexane was purchased from Fluka (Bot, Switzerland). A 50% w v^{-1} aqueous solution of GA was purchased from Sigma-Aldrich. (Stenhem, Geramany). Deionized water (Elga Deionizer, Model LA611, U.K.) was used throughout this research.

Surface Tension of CS and the Surface Energy of the PVA Film
The surface tension of each acidic CS solution was measured by Du Nuoy Ring tensiometry (Kruss 6, Germany), and the surface energy of the PVA film was measured from the contact angles of water and diiodomethane, where the contact angles and the surface energy were calculated by the Young and Fowkes equation,[19] as shown in eq. (1),

$$\gamma_l(1+\cos\theta_1)=2[(\gamma_s^d\gamma_l^d)^{\frac{1}{2}}+(\gamma_s^p\gamma_l^p)^{\frac{1}{2}}] \qquad (1)$$

The total surface energy is the sum of the two contributions of the surface energy, as shown in eq. (2),

$$\gamma_s=\gamma_s^d+\gamma_s^p. \qquad (2)$$

where γ_s is the total surface energy of the substrate, γ_l is the surface tension of the test liquid, γ_s^d and γ_l^d are the dispersion contribution components of the solid surface and test liquid, respectively, γ_s^p and γ_l^p are the polar contribution components of the surface energy and test liquid, respectively, and θ is the contact angle.

Coating of PVA and CS onto the NPK Fertilizer Granules
Based on the material contents, the NPK fertilizer granules (0.8 g) were immersed into 50 mL of a 7% w v^{-1} PVA solution for 5 min and then the granules were removed and air dried in a series of half circular blocks made of aluminum foil at room

Table I. Conditions for the Synthesis of the Poly(AA-co-AM) Layer of the PVA/*Cross*-CS/Poly(AA-*co*-AM) Trilayer-Coated NPK Fertilizer Hydrogel

Ingredient	Contents
AM-to-AA ratios (% mol)	0 : 100, 3 : 97, 6 : 94, 8 : 92, 20 : 80, 50 : 50, 40 : 60, 60 : 40, 70 : 30, 80 : 20, 10 : 90, 97 : 3, 100 : 0
N-MBA (% mol of monomers)	0.005, 0.008, 0.01, 0.015, 0.02, 0.04
APS (% mol of monomers)	0.03, 0.06, 0.10, 0.13, 0.20, 0.24
TEMED (% mol of monomers)	0.03, 0.04, 0.06, 0.1, 0.13, 0.26, 0.52, 1.04, 2.08, 4.16, 8.32

temperature to obtain the PVA-coated fertilizer granules. The dried PVA-coated fertilizer granules were then immersed in a 2% w v^{-1} CS solution in 2% v v^{-1} aqueous acetic acid as above and dried at room temperature for 4 h to vaporize the excess coating solution and moisture, yielding the PVA/CS bilayer-coated NPK fertilizer granules. The water dissolution times of the original NPK fertilizer granules, PVA-coated fertilizer granules, and PVA/CS bilayer-coated fertilizer granules were investigated by placing each fertilizer granule at the specified coating condition in a beaker containing 20 mL deionized water and recording the changes in the granule size from immersion until completely dissolved.

Cross-Linking of the CS-Coated Layer of the PVA/CS Bilayer-Coated Fertilizer Granules

The PVA/CS bilayer-coated NPK fertilizer granules were placed in an aluminum sieve on a Petri dish containing 2 mL of 50% w v^{-1} GA aqueous solution in a closed system of a 2.9 L-chamber for 4 days to yield the PVA/*cross*-CS bilayer-coated fertilizer granules. Their water dissolution times were evaluated in the same manner as that for the PVA- and PVA/*cross*-CS-coated ones above.

Preparation of PVA/*Cross*-CS/Poly(AA-*co*-AM) Fertilizer Hydrogel Granules

The trilayer-coated NPK fertilizer hydrogel granules were prepared from the PVA/*cross*-CS bilayer-coated ones by suspension graft copolymerization of AA and AM to form the poly(AA-*co*-AM) outer layer. The specified amounts of Span 80 and cyclohexane, each at 15 mL, were added into a four-necked flask equipped with a mechanical stirrer, a condenser, and a dropping funnel. The PVA/*cross*-CS bilayer-coated fertilizer granules (1 g) were added into the flask and a fixed amount of APS initiator (Table I) predetermined based on adequate water absorption not less than 20 g g^{-1}, was dropped into the flask and stirred at 180 rpm for 15 min under a nitrogen atmosphere. Next the mixed solution of AM and AA (the total monomer content is shown in Table I) at the specified molar ratio and net amount, and then the N-MBA solution (Table I) were added into the flask followed by TEMED (Table I). The temperature was raised to 70°C in a temperature-controlled water bath and stirred for 45 min maintaining the nitrogen atmosphere and stirring throughout. The mixture was then filtered to remove the unreacted reagents and dried at 50°C in an oven to obtain the

dry PVA/*cross*-CS/poly(AA-*co*-AM) trilayer-coated NPK fertilizer hydrogel. The synthesis conditions are summarized in Table I.

Identification of the Functional Groups on the Different Coated NPK Fertilizer Granules

The functional groups of the PVA/*cross*-CS bilayer-coated NPK fertilizer granules and the poly(AA-*co*-AM) hydrogel outer layer of the PVA/*cross*-CS/poly(AA-*co*-AM) trilayer-coated NPK fertilizer hydrogel were identified by Fourier transform infrared spectroscopy (FTIR, System 2000, Perkin Elmer) after pelleting with KBr (see Table I). The outer (hydrogel) layer of the trilayer-coated NPK fertilizer hydrogel was peeled off, cut, ground, and mixed with dried KBr (analytical grade, Fluka, Switzerland) and the FTIR spectra was investigated with 32 scans at a 4 cm^{-1} resolution.

Surface Morphology of the Different Coated NPK Fertilizers

The NPK fertilizer granules with various coatings and the cross-section of the PVA/*cross*-CS bilayer-coated and the trilayer-coated NPK fertilizer hydrogel granules were photographed by optical microscopy (PM10-AD, Olympus Corporation, Tokyo, Japan). The surface morphology of the dry and swollen outer poly(AA-*co*-AM) hydrogel layer of the trilayer NPK fertilizer hydrogel were analyzed by scanning electron microscopy (SEM) using a model JSM-5410LV (Tokyo, Japan) microscope operating at a voltage of 15 kV for a magnification of 150 times. Each sample was fixed on an aluminum stub and coated with gold before scanning by SEM.

Thermogravimetric Analysis of the Coated NPK Fertilizers

In order to confirm the existence of the different coated layers on the fertilizer, thermogravimetric analysis was conducted. The coated fertilizers weighting from 6.14 to 7.45 mg were each sealed in a pair of aluminum pans. It was subjected to a thermogravimetric analyzer (TG 209 F3 Tarsus - Thermo-Microbalance, NETZSCH-Gerätebau GmbH, Germany) under the nitrogen atmosphere at a heating rate of 10 K min^{-1} from 28 to 600°C. Data were collected and analyses were conducted.

Water Absorbency of the PVA/*Cross*-CS/Poly(AA-*co*-AM) Trilayer-Coated NPK Fertilizer Hydrogel

A 1 g portion of the dry trilayer-coated NPK fertilizer hydrogel was immersed into 200 mL of deionized water and allowed to swell at room temperature. After 1.5, 15, and 24 h, the swollen fertilizer hydrogel was separated from the unabsorbed water by filtering through a 100-mesh sieve aluminum screen for 2 h. The swollen fertilizer hydrogel was weighed and the water absorbency (g g^{-1}) was calculated by eq. (3);

$$W_A = (W_s - W_d)/W_d, \qquad (3)$$

where W_A is the water absorbency as the weight ratio of the dried fertilizer hydrogel, W_s is the weight of the swollen fertilizer hydrogel (g), and W_d is the weight of the dry fertilizer hydrogel (g).

Measurement of the Release of the N, P, and K Nutrients from the Trilayer-Coated NPK Hydrogels

Eight sets of dry trilayer-coated NPK fertilizer hydrogel granules (1 g each) synthesized from the AA : AM ratio of 97 : 3 that gave the highest water absorption, were immersed in different beakers containing 200 mL of deionized water to investigate the

Table II. Mathematical Models Used to Evaluate the Experimentally Determined N, P, and K Release Kinetics

Model	Equations	Y	X
Zero-order	$Q_t = Q_0 + k_0 t$	Q_t	t
First order	$\log Q_t = \log Q_0 + kt/2.303$	$\log Q_t$	t
Higuchi	$Q_t = k_H t^{1/2}$	Q_t	$t^{1/2}$
Baker-Lonsdale	$3/2[1 - (1 - F_t)^{2/3}] - F_t = kt$	$3/2[1 - (1 - F_t)^{2/3}] - F_t$	t
Hixson-Crowell	$(1 - F_t)^{1/3} = 1 - kt$	$(1 - F_t)^{1/3}$	t
Korsmeyer-Peppas	$M_t/M_\infty = kt^n$	log% cumulative drug release	Log t
Ritger-Peppas	$\ln F_t = \ln k + n \ln t$	Ln F_t	Ln t

Q_t and Q_0 are the amounts of material released (g g^{-1}), t is release time and at $t = 0$, k_0 is the zero-order rate constant (concentration/time). The term k is the first-order rate constant (h^{-1}), k_H is the Higuchi dissolution constant and F_t is the fraction of material released at time t. In the Korsmeyer-Peppas model, M_t/M_∞ is the fraction of material released at time t, k is the release rate constant; n is the diffusion type or index of release exponent, and t is the release time.

release of the NPK fertilizer components at ambient conditions. After immersion for the indicated time (1, 3, 5, 10, 15, 20, 25, and 30 days), 100 mL of supernatant was removed for analysis of the released N, P, and K nutrient contents. The granules in each beaker were then removed, washed with distilled water, and then dried at room temperature overnight to estimate their residual N, P, and K contents. The released amount of the N nutrient in the supernatant was analyzed by the Kjeldahl method,[9] while the P and K nutrients were measured by spectrophotometry at an absorption wavelength of 880 nm and atomic absorption spectrophotometry at an absorption wavelength of 766.5 nm, respectively. At least three replications were performed for each type of fertilizer hydrogel. The amount of the NPK release was calculated from eq. (4);

$$\%\text{nutrient release} = \frac{(\text{Nut}_0 - \text{Nut}_t) \times 100}{\text{Nut}_0} \qquad (4)$$

where Nut_0 is the initial amount of the N, P, and K nutrients in the obtained trilayer-coated NPK fertilizer hydrogel and Nut_t is the amount of the N, P, and K nutrients released into the water in time t.

The release of the N, P, and K nutrients from the trilayer-coated NPK fertilizer hydrogel having a water absorption value of 233 ± 5 g g^{-1}, synthesized from the AA : AM ratio of 97 : 3, 0.13% mol of initiator, 0.13% mol of coinitiator and 0.01% crosslinker at 70°C for 1 h reaction time, were each analyzed for goodness of fit with the mathematical models of: Zero-order kinetics; first-order kinetics; Higuchi equation (square-root of time equation),[20,21] Baker-Lonsdale equation, Hixson-Crowell equation, Korsmeyer-Peppas equation,[22] and Ritger-Peppas equation,[23,24] as summarized in Table II. Linear regression was applied for the calculation of the correlation coefficient (R^2) as a measure of the goodness of fit and to obtain the best fit line from which the slope (n) was used as an exponent that characterizes the mechanism of fertilizer nutrient releases.

RESULTS AND DISCUSSION

PVA and CS Coatings on the NPK Fertilizer Granules
The coating solution must possess a lower surface tension than that of the substrate to be coated or, in other words, a higher surface energy substrate can be wetted and coated by a coating solution with a lower surface tension. The surface tensions of the M_W 100 and 200 kg/mol CS solutions were found to be 56.4 ± 1 and 61.0 ± 1 mN m^{-1}, respectively, and so the higher M_W CS gave a slightly (1.08-fold) higher surface tension. Since the surface energy of the PVA film (66.7 ± 1 mN m^{-1}) was higher than that of either M_W CS solution, then both CS solutions could be used as a coating solution on the PVA film due to their wetting and spreading ability on the PVA film. In this study, however, the lower M_W (100 kg mol^{-1}) CS was found to be unsuitable for coating the NKP fertilizer granules because in preliminary trials it was found to let more water penetrate into the fertilizer due to its thinner film forming characteristics. Thus, the 200 kg mol^{-1} M_W CS was used in this research.

The original (uncoated) NPK fertilizer granules dissolved in water within 12 ± 2 min ($n = 30$), while the PVA-coated and the PVA/CS bilayer-coated ones dissolved 4.5- and 6.2-fold slower than that of the uncoated fertilizer granules, respectively, and the PVA/*cross*-CS bilayer-coated ones dissolved 11.5-fold slower in water (138 ± 2 min) and to a lesser net extent. Thus, the *cross*-CS layer effectively reduced the rate of penetration of water into the fertilizer granule, while the increased number and/or type of coating layers increased the water dissolution time as several coating layers allowed a more effective control (retardation) of the incoming water to penetrate into the fertilizer and to potentially reduce the wastage of fertilizer.

Morphology of the Different Coated NPK Fertilizer Granules
Representative optical microscopy images (150× magnifications) of individual granules of the NPK fertilizer at various stages of treatment are shown in Figure 1. The uncoated NPK fertilizer granules [Figure 1(a)] had the smallest size compared to those of the differently coated fertilizers. The PVA-coated fertilizer granules [Figure 1(b)] had a whiter and smoother surface, while although the PVA/CS bilayer-coated granules [Figure 1(c)] were of a similar size to the PVA-coated ones their surface was whiter and rougher. The PVA/*cross*-CS bilayer-coated fertilizer granules [Figure 1(d)] had a darker, reddish brown surface, which is because the GA vapor was deposited on and crosslinked the CS-coated fertilizer and so changed its surface color from white to a slight reddish brown color. The surface of the trilayer-coated fertilizer hydrogel [Figure 1(e)] synthesized with
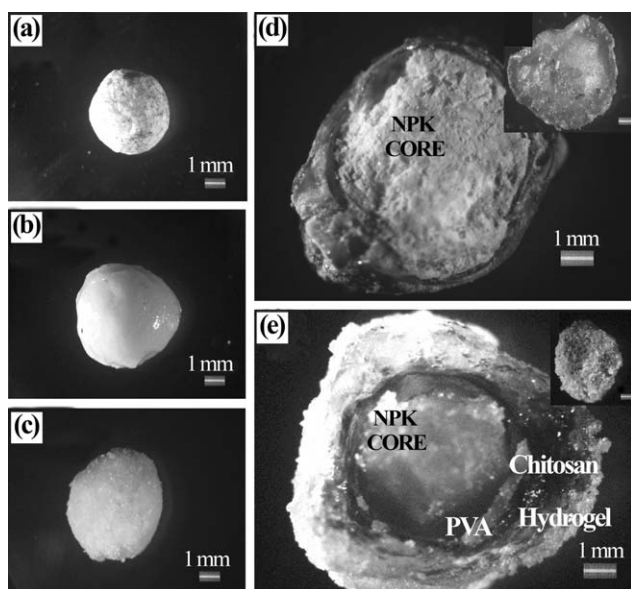
Figure 1. Optical microscope images (×150 magnification) of the various NPK fertilizer granules: (a) original (uncoated), (b) PVA-coated, (c) PVA/CS bilayer-coated, and a cross-section of the (d) PVA/*cross*-CS bilayer-coated, and (e) PVA/*cross*-CS/poly(AA-*co*-AM) trilayer-coated hydrogel from synthesized condition of AA : AM at 97 : 3 molar ratios. The inset small figures inserted in (d) and (e) are the non-cross-section of the two figures themselves.

AA : AM = 97 : 3 was porous (Table I), which is characteristic of poly(AA-*co*-AM) hydrogels. The cross-sectional appearance of the PVA/*cross*-CS bilayer-coated fertilizer and the related trilayer-coated fertilizer hydrogel (Figure 1) revealed that the *cross*-CS layer could likely interact with the poly(AA-*co*-AM) hydrogel layer, and this is presumably via a radical chain grafting reaction.

The SEM analysis of the dry poly(AA-*co*-AM) hydrogel layer from the trilayer-coated NPK fertilizer hydrogel, a representative in the series of fertilizer hydrogel, revealed the porous nature of this outer layer [Figure 2(a)]. When pieces of this outer poly(AA-*co*-AM) hydrogel layer were immersed in deionized water, the porous structure of the swollen hydrogel layer became elongated [Figure 2(b)]. Progressive swelling of copolymer hydrogels leads to considerable structural changes, such as in the mobility of the macromolecular chains, macromolecular relaxations and changes in the porous structure in terms of their shape and size. Thus, as the water passed through the hydrogel, it absorbed the incoming water and swelled. The hydrogel was then deformed, eroded, and transferred the absorbed water inward to reach the fertilizer, the release rate of which was controlled via these hydrogel structures. In other words, the hydrogel layer retarded the incoming water from reaching the fertilizer and so reduced the leaching of the N, P, and K nutrients out of the NPK fertilizer granules.

The characterization of multilayer-coated NPK compound fertilizer hydrogel by thermogravimetric analysis also can be carried out in order to confirm that PVA, cross-linked CS, and hydrogel were coated on the fertilizer. TGA curves of various layers of fertilizer deposition are shown in Figure 3. The thermal degradation of PVA-coated fertilizer took place in four stages [Figure 3(a)]. The first stage was the loss of water or moisture vaporization at 83.3°C with a mass loss 1.32%. The second and third stages were due to thermal degradation of PVA molecules at 220.1 and 296.5°C with a mass loss of 17.67 and 17.01%, respectively.[25] The final stage might be attributed to by-product generated from PVA during the TGA thermal degradation process at 497.8°C with a mass loss of 9.91%. TGA curve of the PVA/CS bilayer-coated fertilizer is shown in Figure 3(b). The first stage was thermal degradation of CS and PVA molecules at 197.9, 227.8, and 263.8°C with a mass loss of 34.47%.[25,26] The second stage might be attributed to by-product from PVA at 438.8°C with a mass loss of 7.49%.[25] The final stage was due to decomposition of CS at 587.7°C with a mass loss of 6.30%.[26] TGA curve of the PVA/*cross*-CS bilayer-coated fertilizer had four stages as shown in Figure 3(c). The first stage was moisture vaporization at 86.6°C with a mass loss of 1.32%. The second stage showed a mass loss of 38.12% at 232.3°C that could be ascribed to the thermal degradation of PVA molecules[25] and cross-linked CS. The loss of cooperative H-bonding along the CS backbone occurred due to cross-linking effects. Thus, cross-linked CS had the lower decomposition temperature than that of non-crosslinked CS.[27] The third stage at 436.8°C with a mass loss of 11.50% could be attributed to by-product from PVA. The final stage at 589.5°C with a mass loss of 4.24% might be due to decomposition of CS. TGA curve of the PVA/*cross*-CS/poly(AA-*co*-AM)-coated NPK fertilizer hydrogel is shown in Figure 3(d). The first stage could be water loss at 75.4°C with a mass loss of 7.03%, which could not be removed completely from the hydrogel layer. The second stage showed a mass loss of 7.03% at 239.9°C due to thermal degradation of PVA and cross-linked CS. The final stage started at approximately 300 up to 590°C with a mass loss of 42.83%. The endothermic peak at 336.9°C was decarboxylation of poly(AA-*co*-AM).[28] The small endothermic peak at 414.8°C might be due to decomposed by-product generated from PVA. The nitrogen nutrient in the form of ammonium sulfate and phosphorus nutrient in the form of phosphorus pentoxide that normally decomposes above 250°C and 360°C, respectively, might overlap with the decompositions of polymers in the coating materials. Potassium nutrient in the form of potassium chloride melts and decomposes over 770°C.
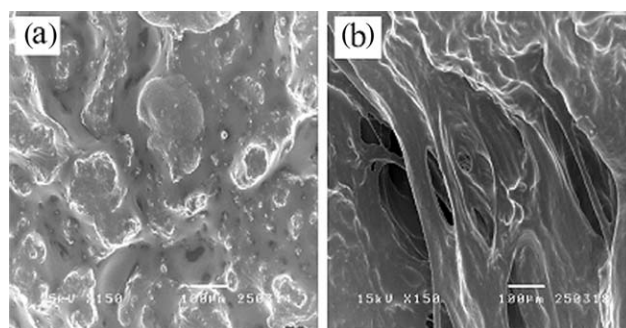

Figure 2. SEM micrographs of the poly(AA-*co*-AM) hydrogel outer layer from the synthesized condition of AA : AM at 97 : 3 molar ratios in (a) a dry condition and (b) after water swelling.
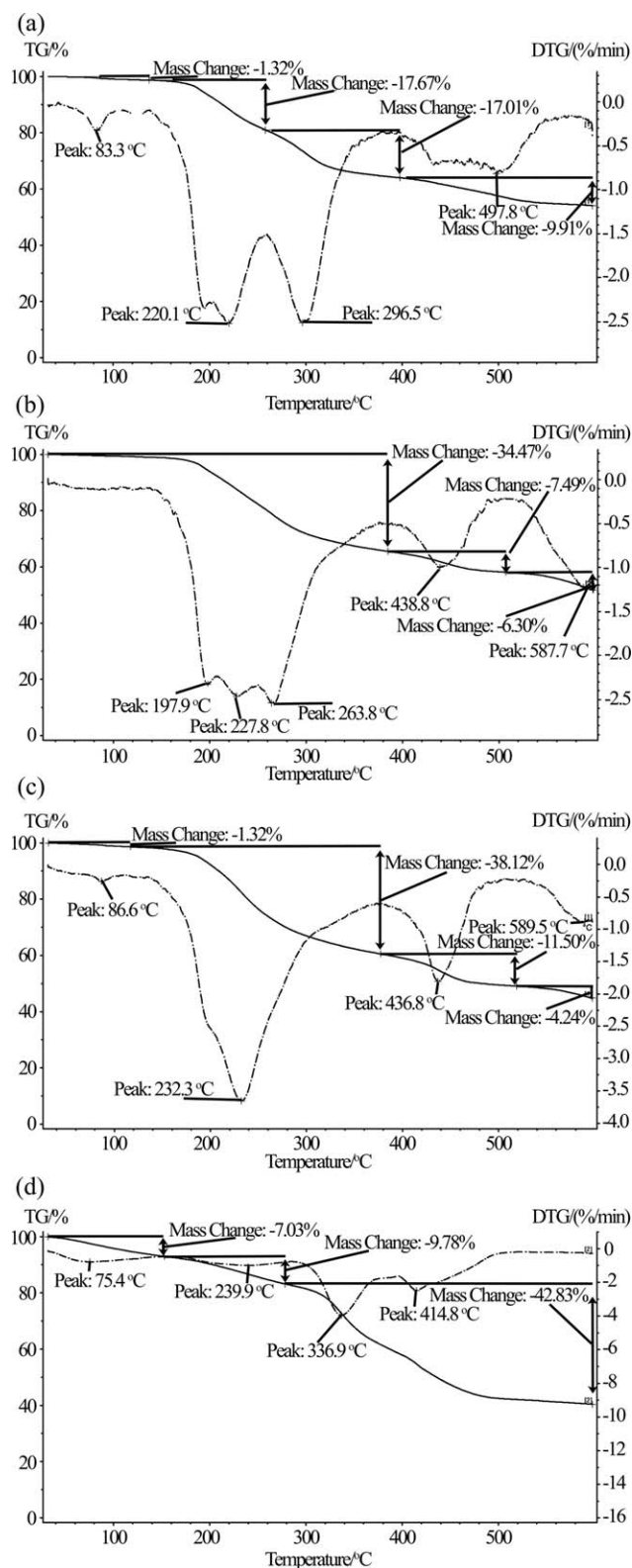
Figure 3. Thermal gravimetric analyses of the NPK compound fertilizer coated with (a) PVA-single layer-coated, (b) PVA/CS bilayer-coated, (c) PVA/*cross*-CS bilayer-coated, and (d) PVA/*cross*-CS/poly(AA-*co*-AM) trilayer-coated hydrogel.

Identification of the Functional Groups of the Hydrogel Outer Coating Layer by FTIR Analysis

Figure 4 depicts the spectra of four stages of NPK fertilizer. The FTIR spectra of the GA solution and two types of the bilayer-coated NPK fertilizer revealed the characteristic peaks of GA at 2873 and 1713 cm^{-1}, assigning to —C—H and —C=O stretching of the aldehyde group, respectively [spectrum (a)]. The —N—H bending (amide) peak of CS in the PVA/CS bilayer-coated fertilizer was found at 1637 cm^{-1} [spectrum (b)], whereas this was absent in the PVA/*cross*-CS bilayer-coated fertilizer [spectrum (c)]. The stronger intensity of the peak at 1635 cm^{-1} in the PVA/*cross*-CS bilayer-coated fertilizer samples corresponded to the —C=N-stretching vibration of the imine group of the Schiff base, which was formed from the reaction between the —CHO groups of GA and the —NH$_2$ groups of CS. This was due to the presence of the acetal group formed from the reaction between the —CHO groups of GA and —OH groups of CS, respectively.[18,29] The FTIR analysis supports that the CS-coated outer layer of the PVA/*cross*-CS bilayer-coated fertilizer was indeed cross-linked by the GA vapor.

The spectrum of the outer poly(AA-*co*-AM) layer of the trilayer-coated fertilizer hydrogel exhibited peaks at 3430, 2926, and 1647 cm^{-1}, which correspond to the —N—H, —C—H, and —C=O stretching of the AM moiety, respectively [spectrum (d)]. It also showed peaks at 1739 and 1093 cm^{-1}, assigning to the —C=O and —CO—O— stretching of the AA moiety, respectively.[3] This then supports that the outer coating material of the trilayer-coated NPK fertilizer hydrogel was poly(AA-*co*-AM).

Effect of Varying the Reagent Proportions in the *In Situ* Poly(AA-*co*-AM) Synthesis on the Water Absorbency of the Obtained Trilayer-Coated NPK Fertilizer Hydrogel

AA-to-AM Monomer Ratios. The water absorbency of the trilayer-coated NPK fertilizer hydrogel at a 24-h swelling time
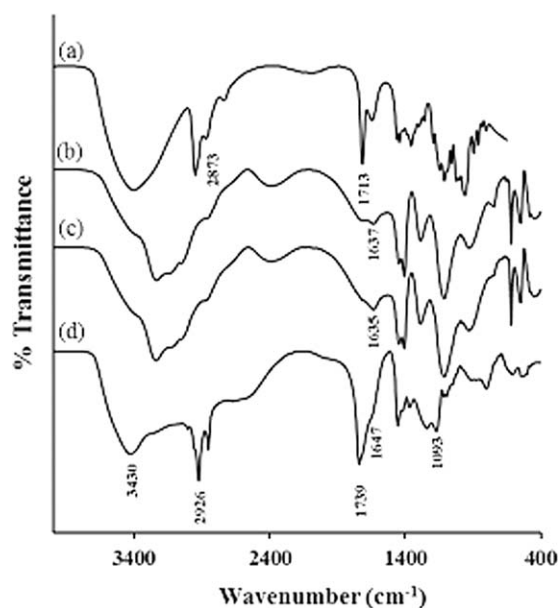

Figure 4. FTIR spectra of: (a) GA, and the NPK fertilizer granules after covering with (b) PVA/CS bilayer, (c) PVA/*cross*-CS bilayer, and the (d) poly(AA-*co*-AM) outer layer from the PVA/*cross*-CS/poly(AA-*co*-AM) trilayer-coated hydrogel from the synthesized condition of AA : AM at 97 : 3 molar ratios.
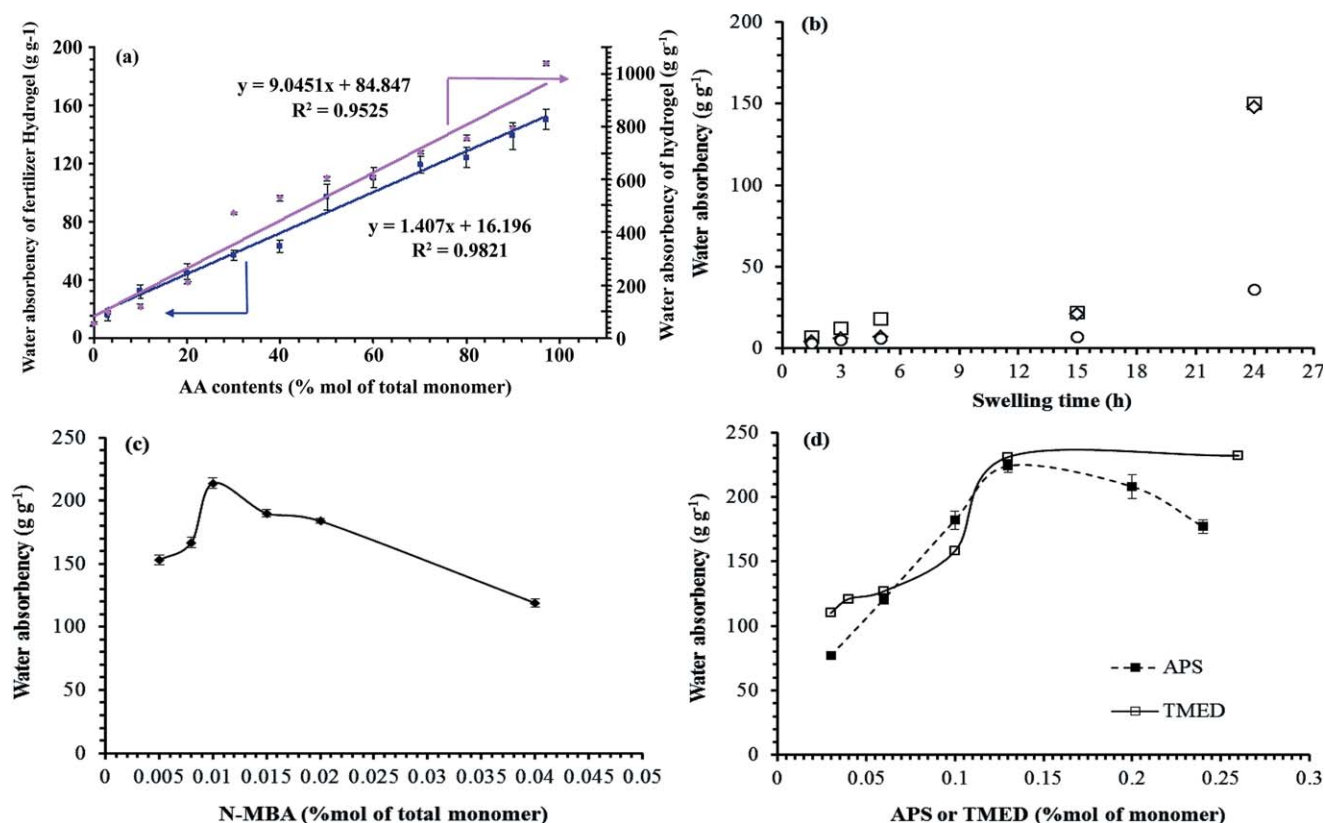
Figure 5. Water absorbency of the PVA/cross-CS/poly(AA-co-AM) trilayer-coated hydrogel granules after *in situ* poly(AA-co-AM) formation with different proportions of (a) AA (after a 24 h immersion in water), (b) selected AA : AM molar ratios at 97 : 3 (□), 94 : 6 (◇), and 92 : 8 (○) over a 24 h swelling time, (c) N-MBA, and (d) APS or TEMED from the synthesized condition of AA : AM at 97 : 3 molar ratios. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

gradually increased with increasing AA contents [Figure 5(a)], due to the incorporation of more hydrophilic moieties. The higher the hydrophilicity, the greater the hydrogel expansion leading to a higher water absorbency.[3,30] A small increase in the water absorbency was observed after a short time of water immersion, when the poly(AA-co-AM) hydrogel outer layer was swollen and expanded, becoming larger compared with the whole trilayer-coated fertilizer granules. To confirm the effect of poly(AA-co-AM) on the water absorbency of the trilayer-coated NPK fertilizer hydrogel, neat poly(AA-co-AM) hydrogels were synthesized under the same conditions as that for the trilayer-coated fertilizer hydrogels. The water absorbency of the neat poly(AA-co-AM) hydrogel granules was found to be at least seven fold higher than those of the trilayer-coated NPK fertilizer hydrogels from the same AA : AM ratio [Figure 5(a)], which indicated that the water absorbency of the poly(AA-co-AM) layer was also affected by components of the fertilizer hydrogel, such as the ionic strength of the K^+ cation.

With respect to time, the swelling of the NPK fertilizer hydrogel at various AA contents was minimal over the first 15 h immersion in water and thereafter the water absorbency and swelling markedly increased (over six fold of that at 15 h) by 24 h immersion in water [Figure 5(b)]. This is because the fertilizer hydrogel absorbs water slowly and cannot reach the equilibrium water absorbency within 24 h. The water absorbency of the

trilayer-coated NPK fertilizer hydrogels synthesized with an AA content of 97 and 94% mol of total monomer were similar after 24 h of immersion in water at 150 ± 1 and 148 ± 1 g g^{-1}, respectively, which was at least four fold higher than that obtained with a total AA content of 92% mole of total monomer (36 ± 1 g g^{-1}).

N-MBA Cross-Linker Content. When the N-MBA cross-linker content in the synthesis of the poly(AA-co-AM) coating layer was increased from 0.005 to 0.01% mole of monomers, the water absorbency of the obtained trilayer-coated NPK fertilizer hydrogel increased [Figure 5(c)]. This was due to the formation of the cross-linked poly(AM-co-AA) chains. However, at N-MBA contents above 0.01% mole of monomers the water absorbency decreased, reaching a 1.81-fold lower level than at 0.01% at a N-MBA concentration of 0.04%. This is because of the increased rigidity of the cross-linked chains that then reduced the expansion of the polymer chains at the outer layer of the fertilizer hydrogel.[10,31] Accordingly, the suitable N-MBA cross-linker content was selected as 0.01% mole of monomers since this produced the highest water absorbency (216 ± 7 g g^{-1}) after a 24 h immersion in water.

Initiator (APS and TEMED) Content. When a relatively low APS content (0.03% mole based on the monomers) was used in the synthesis of poly(AA-co-AM) coating layer, the water

Table III. Releasing Properties of Compound Fertilizer Hydrogel Nutrient N, K, and P Release Levels from the PVA/Cross-CS/Poly(AA-co-AM) Trilayer-Coated NPK Compound Fertilizer Hydrogel

Immersion	Number of days	Cumulated percentage nutrient release (milligram per liter) from compound fertilizer hydrogel		
		N	P	K
	1	21.1 ± 12	18.3 ± 3	7.4 ± 3
	3	31.8 ± 6	21.3 ± 3	9.3 ± 5
	5	33.5 ± 5	22.5 ± 4	9.7 ± 4
	10	39.5 ± 8	26.8 ± 5	11.0 ± 4
	15	42.1 ± 7	28.5 ± 4	13.2 ± 5
	20	48.9 ± 9	29.2 ± 4	14.9 ± 6
	25	73.0 ± 24	45.5 ± 3	21.1 ± 8
	30	83.9 ± 18	62.3 ± 12	36.2 ± 15
Kinetics models				
Korsmeyer-Peppas	R^2	0.9716	0.9838	0.9462
	n	0.2574	0.1642	0.3696
	Release factor	22.1	18	7.2
Ritger-Peppas	R^2	0.9716	0.9838	0.9462
	n	0.2574	0.1642	0.3696
	Release factor	0.22	0.18	0.72

absorbency of the obtained trilayer-coated NPK fertilizer hydrogel was low [Figure 5(d)]. The water absorbency increased with increasing APS contents from 0.03 to 0.13% mole of monomers, reaching a 2.93-fold higher level than at 0.03% at an APS content of 0.13%. However, at APS contents above 0.13% mole of monomers the water absorbency decreased. Thus, the highest water absorbency observed after a 24 h immersion in water (227 ± 5 g g^{-1}) was found at an APS initiator content of 0.13% mole of the monomer content. Presumably, at lower APS contents only a few radicals were generated, resulting in short polymer chains. Likewise, at APS contents higher than 0.13%, too many radicals were generated yielding short polymer chains again due to recombination of the radicals. Hydrogels with short polymer chains cannot swell as much due to the lower anionic repulsion by the small amount of carboxylate groups.

In the APS and TEMED redox initiated polymerization, TEMED generates the electrons to reduce APS, resulting in a sufficient level of free radicals to produce longer polymer chains and so a higher water absorbency of the obtained hydrogel.[32] Here, the TEMED content in the poly(AA-co-AM) synthesis was also found to significantly affect the water absorbency of the obtained trilayer-coated NPK fertilizer hydrogel. The optimal TEMED content was 0.13% mole of monomers (equal to that of the APS), giving a maximum observed water absorbency of 233 ± 5 g g^{-1} [Figure 5(d)]. At lower TEMED contents, the amount of activated TEMED molecules was insufficient to accelerate the production of hydroxyl radicals from the APS, resulting in rather short chains being formed in the poly(AA-co-AM) hydrogel.

Controlled Release of the NPK Nutrients from the Trilayer-Coated NPK Fertilizer Hydrogel

The N, P, and K nutrient contents of the uncoated NPK fertilizer granules were 123 ± 25, 292 ± 5, and 256 ± 0.3 mg, respec-

tively, giving a calculated N : P : K weight ratio in the NPK fertilizer hydrogel of approximately 1 : 2.9 : 2.6. When compared to the factory supplied data of 1 : 3 : 3, the calculated N and P nutrient levels were very close to the factory specification, while the amount of K was slightly lower.

The trilayer-coated NPK fertilizer hydrogel did not dissolve completely in water within 30 days of immersion, but the level of released N, P, and K salts from the granules increased with an increasing immersion time (Table III and Figure 6). For example, after 1 day of immersion in water, the amount of released N, P, and K nutrients were 26.2 ± 13, 53.5 ± 11, and 18.9 ± 8 mg L^{-1}, respectively, while they were three- to four fold higher at 103.9 ± 22, 182 ± 30, and 92.7 ± 32 mg L^{-1}, respectively, after 30 days of immersion in water [Figure 6(a)]. The release of the P nutrient was the highest compared with that for N and K. In terms the percentage total release after 30 days of immersion in water, the nutrient release order was N ($83.9 \pm 18\%$) > P ($62.3 \pm 12\%$) > K ($36.2 \pm 15\%$) as shown in Figure 6(b).

Interestingly, the K content in the unmodified compound fertilizer was 2.6-fold higher than that of N but its percentage release was the lowest ($36.2 \pm 15\%$). To explain this phenomenon, the ionic mobility and the electronic and steric effects of the K$^+$ and NH$_4^+$ ions were compared. Their reported ionic mobilities are very similar at 1.000 and 1.001 m^2 s^{-1} V^{-1}, respectively,[33–35] and they have a similar ionic mobility and the same positive charge value ($+1$). However, the size of K$^+$ (1.33Å) is smaller than that of NH$_4^+$ (1.47Å), and so the K$^+$ ions have a higher surface area charge density to interact with the negatively charged carboxylate ion of the poly(AA-co-AM) hydrogel layer. To test this postulation, the water absorbency of the neat poly(AA-co-AM) hydrogel synthesized with an AA : AM molar
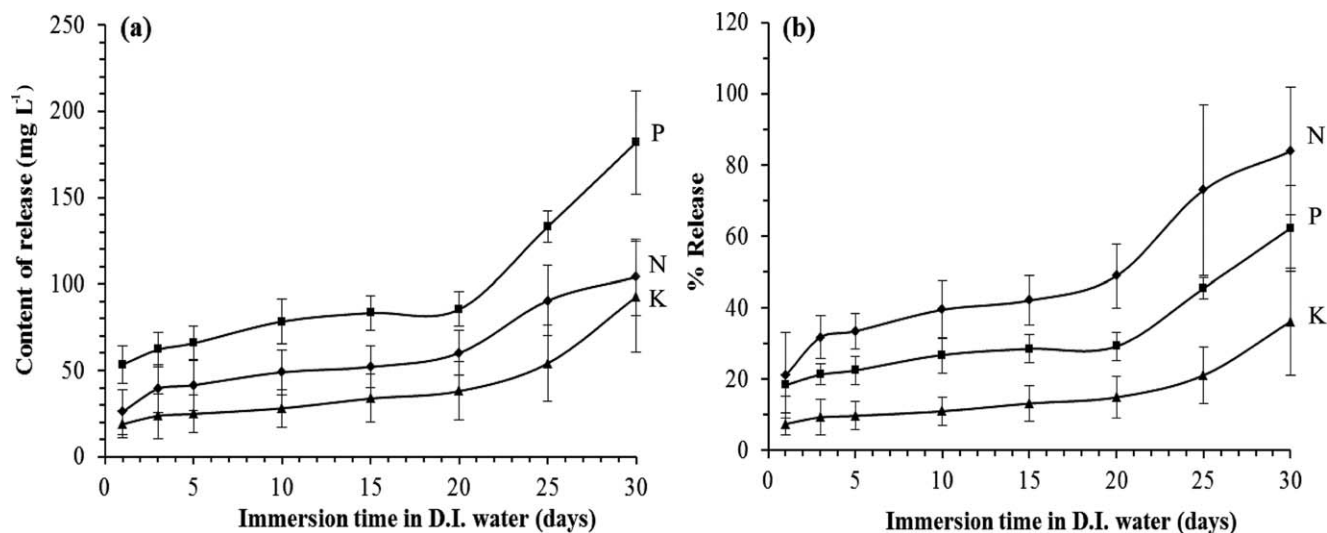
Figure 6. Controlled release of the N, P, and K nutrients from the PVA/*cross*-CS/poly(AA-*co*-AM) trilayer-coated NPK fertilizer hydrogel from the synthesized condition of AA : AM at 97 : 3 molar ratios. (a) The released amounts and (b) % total released proportion of the N, P, and K nutrients with increasing immersion time in deionized water.

ratio of 97 : 3 was measured in water, 0.1 mM potassium chloride solution, and 0.1 mM ammonium chloride solution, the latter two being at an equal ionic strength. The hydrogel water absorbency (914 ± 23 g g^{-1}) was found to decrease to 527 ± 43 and 225 ± 54 g g^{-1} in the ammonium chloride and potassium chloride solutions, respectively. That the water absorbency decreased by 2.34-fold in the potassium chloride solution compared to that in the ammonium chloride solution, even though both ions had the same +1 positive charge, likely reflects the smaller atomic size of K$^+$ (compared to NH$_4$$^+$) resulting in more ionic interactions with the negatively charged carboxylate ion of poly(AA-*co*-AM). The lower repulsion force of the hydrogel chains would then result in lower water absorbency. Accordingly, the low percentage of K release could reflect the ionic interaction between the K$^+$ ions and the hydrogel layer during the diffusion of K$^+$ from the inner to the outer layer of the trilayer-coated NPK fertilizer hydrogel.

Kinetics of the N, P, and K Nutrient Release from the Trilayer-Coated NPK Fertilizer Hydrogel

The release kinetics of the N, P, and K nutrients from the trilayer-coated NPK fertilizer hydrogel were analyzed and compared by their respective correlation coefficients to the models and equations outlined in Table II, so as to analyze and predict the mechanisms of their release. The zero order, first order, Higuchi, Hixson-Crowell, and Baker-Lonsdale models all gave poor curve fittings with relatively low R^2 values for the three nutrients. Accordingly, no further studies with these models were considered. When the Ritger-Peppas [Figure 7(a)] and Korsmeyer-Peppas [Figure 7(b)] models used only the M_t/M_∞ data < 0.6 (60%), they were found to both give the highest linearity with correlation coefficients (R^2) of 0.9716, 0.9838, and 0.9462 for the N, P, and K release, respectively, although the amount of K released after 30 days of immersion in water was far below 60%. The diffusion indices (n), as calculated from the slopes, of both the N and P release mechanisms from the NPK

fertilizer hydrogel were the same for both the Ritger-Peppas and the Korsmeyer-Peppas models at 0.2574 and 0.1642 (n values are smaller than 0.5), respectively (Table III). The diffusion index decreased considerably, which is characteristic of pseudo-Fickian behavior or a two-stage sorption, and was probably caused by the ionic interaction between the negative charge of CS and the positive charge of the K$^+$ ion.

Considering the release factors in both models (Table III), the values from the Ritger-Peppas model were only two orders of magnitude lower than those from the Korsmeyer-Peppas model,
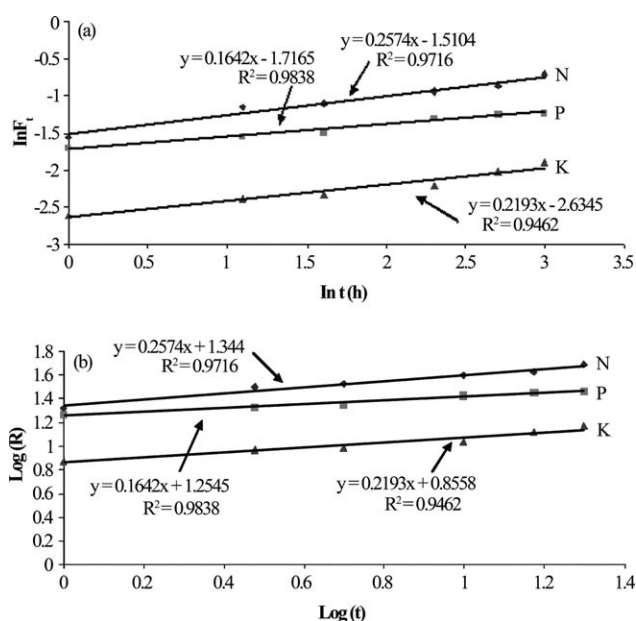

Figure 7. Kinetics of the release of the N, P, and K nutrients from the PVA/*cross*-CS/poly(AA-*co*-AM) trilayer-coated fertilizer hydrogel from the synthesized condition of AA : AM at 97 : 3 molar ratios, based on (a) the Ritter-Peppas and (b) Korsmeyer-Peppas models.

which is due to the differences in their expression terms (ln vs. log). The release factors of the three types of nutrients conform to this release order and, therefore, the release of the compound fertilizer obeys both models for each nutrient release. That the experimental results conformed to both models is reasonable since they both preserve the same mathematical meaning and interpretation of the results.

The NPK fertilizer was coated with three different materials, PVA and cross-CS followed by a thicker poly(AA-co-AM) hydrogel layer, which resulted in the complicated N and P nutrient release mechanisms from the encapsulated fertilizers. As water from the ambient environment enters the compound fertilizer, the diffusion rate through the glassy polymer is normally very low. First, the water has to plasticize the copolymer hydrogel and the PVA/cross-CS bilayer coating and reduce the glass transition temperature to that equal to the ambient temperature. At this stage, the outer hydrogel swells almost completely while the core NPK fertilizer components partially dissolve into the free solution to form a higher viscosity one. The higher viscosity solution in the pores served to retard the diffusion of the nutrients at the early stage of release. At the later stages of release, the nutrient solution becomes dissipated and resistance to diffusion is decreased.[23] The net effect is a decreased release rate, which is normally observed when the nutrient concentration in the fertilizer is decreased and only small amounts of nutrient penetrate out of the outer layer of the hydrogel. Under the two-stage sorption/diffusion process, the diffusion of the N and P nutrients decreased considerably.

CONCLUSIONS

A novel trilayer-coated NPK fertilizer hydrogel was successfully synthesized by coating NPK granules first with PVA and then with CS, cross-linking of the CS layer by GA vapor deposition to form crosslinked-CS and then in situ formation of the outer poly(AA-co-AM) layer. OM images and TGA analyses confirmed the coexistence of the multi-coating layers. The crosslinking of the CS layer increased the level of water penetration, while the increased number and/or type of coated layers increased the water dissolution time. The proportions of all the reagents used in the in situ inverse suspension copolymerization of AA and AM to form the final poly(AA-co-AM) coating affected the water absorbency of the obtained trilayer-coated NPK fertilizer hydrogel. The N nutrient level released from the NPK fertilizer granules within 30 days of water immersion was highest for N and lowest for K. The controlled release of the N and P nutrients from the trilayer-coated NPK fertilizer hydrogel obeyed both the Korsmeyer-Peppas and Ritger-Peppas models with pseudo-Fickian characteristics. Thus, the PVA/cross-CS/poly(AA-co-AM)-coated NPK fertilizer hydrogel resulted in fertilizer granules with more suitable levels of water absorbency and controlled release of the N, P, and K nutrients from the NPK fertilizer

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