1-Naphthylacetic-Acid-Functionalized Polyacrylate-Coated Urea with Dual Controlled-Release Properties

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ABSTRACT: Esters derived from 1-naphthylacetic acid (NAA) and polyacrylate were synthesized and a dual controlled-release formulation was developed by coating fertilizers with these esters. FT-IR, ^{1}H NMR, TGA, and DSC were used to characterize the synthesized polymers, and the mechanical properties were also tested. Urea granules were coated with NAA esters, and the release rates of urea from the coated granules in water were measured. NAA release from the esters was performed in different buffer solutions and in soil. The results showed that the coated fertilizers were able to release urea in a controlled pattern and that NAA could be slowly released from membranes of the esters in both buffer solutions and in soil through hydrolysis. The coated fertilizer's availability could last more than 28 days and that of NAA could last more than 12 months, which suggested that the prepared CRF possessed dual controlled-release of urea and NAA. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 129: 559–567, 2013

INTRODUCTION

Agrochemicals such as fertilizers, herbicides, pesticides, and plant-growth regulators (PGRs) are essential for agriculture. However, excessive use of agrochemicals as a result of the pressures of growing population and food demand is of great concern in terms of human health and environmental risks.[1,2] Controlled-release formulations (CRFs) for agrochemicals are able to address problems such as leaching, volatilization, and surface migration because of their sustained-release properties,[1–5] and also perform better than conventional formulations at lower dosages.[2,5–7]

There are three types of CRFs for fertilizers: inorganic low-solubility compounds such as metal ammonium phosphates; organic-nitrogen low-solubility compounds such as urea–formaldehyde; and fertilizers with physical barriers, such as polymer-coated fertilizers.[2] Polymer coating on solid fertilizer granules is the most common controlled-release method, and the coated fertilizer is resistant to runoff and leaching.[1] Polyolefin is most frequently used as coatings.[3] Not only fertilizers, but also PGRs should be applied in controlled patterns. One of the biological shortcomings in the application of PGRs is the very narrow concentration, ranging over which PGRs are effective. The response is characterized by a sharp rise and drop in biological activity, moving on to a negative response with a further increase of PGR, and appearance of herbicide-like effects.[8]

Among PGRs, NAA is widely used in agriculture for rooting of cuttings, inhibition of fruit-set, fruit abscission, and induction and control of flowering. NAA was loaded in a matrix of an inorganic Zn–Al-layered double-hydroxide using a self-assembly technique, and the mechanism of controlled release was interpreted on the basis of the ion-exchange process between the NAA anions intercalated in the lamellar host and nitrate/hydroxyl anions in the aqueous solution.[9] However, the mechanism of hydrolysis of esters of NAA for its sustained release has drawn more attention because the polymeric derivatives are biologically active after releasing NAA by hydrolysis, and their effectiveness is longer than that of NAA.[8–13] The sustained-release periods of NAA esters ranged from months to years, depending on the types and structures of the copolymers.[9–12]

The preparation of polymeric esters of NAA derived from epoxy-bearing random copolymers requires harsh conditions with temperatures higher than 140°C.[14] Halogenated polymers were used in other studies to synthesize polyesters of NAA,[13,15,16] but they were impractical because of their relatively high price and environmental issues related to the presence of halogens. Hydroxy-bearing polymers are the ideal reagents for synthesizing esters of NAA, such as hexyl isomer alcohols,[10] modified amylase,[11] poly(ether-amide)s bearing hydroxyl side groups,[12] and poly(vinyl alcohol).[13] In our previous work, modified chitosan was used to prepare a novel formulation for sustained

Table I. Experimental Details of Poly(BMA–MMA–HEA)s

Run	Code	MMA (wt %)[a]	BMA (wt %)[a]	HEA (wt %)[a]	BPO (wt %)[b]	EA (v %)[c]
1	P0	25	75	0	0.9	200
2	P1	25	72.5	2.5	0.9	200
3	P2	25	70	5	0.9	200
4	P3	25	67.5	7.5	0.9	200
5	P4	25	65	10	0.9	200

[a]Weight ratio vs. total monomers, [b]Weight ratio vs. total monomers, [c]Volume ratio with total monomers.

release of NAA,[17] but the previous studies were limited to NAA-releasing behaviors. Thus, the polymers possessed only one property of controlled-release of NAA.

Multifunctional CRFs are intriguing because several functions can be achieved using one formulation, so they are labor-saving and economical. The most widely used CRFs are controlled-release fertilizers combined with water retention, prepared by incorporation or coating.[18–22] A nano-hybrid system of the phytohormone gibberellic acid, using an inorganic Mg–Al-layered double-hydroxide material, was formulated with the multifunctions of gibberellic acid controlled-release and slow-rate degradation.[23] To the best of our knowledge, there are no published results on multifunctional CRFs with regard to controlled release of both NAA and nutrients.

Both fertilizers and NAA need to be provided in a controlled pattern to minimize potential losses, biotoxicity, and environmental pollution. In this study, a novel multifunctional CRF was prepared by coating urea with polyacrylate with pendant NAA side groups in a fluidized bed, and was assumed to release urea and NAA in a controlled pattern. The polyacrylate coating provided a barrier to contact between urea and water, which could regulate the release rate of urea, and the polyacrylate with NAA pendant side groups could release NAA in a sustained and controlled manner. The release rate of urea in water and the release behaviors of NAA in buffer solutions and in soil were investigated to verify the dual controlled-release properties of the prepared coated fertilizers.

EXPERIMENTAL

Materials

N-butyl methacrylate (BMA) was obtained from Sigma–Aldrich (St. Louis, MO). Methyl methacrylate (MMA) was purchased from Beijing Yili Fine Chemicals (Beijing, China). The 2-hydroxyethl acrylate (HEA) and 4-(dimethylamino) pyridine (DMAP) were purchased from Alfa Aesar (Haverhill, MA). NAA and N,N-dicyclohexylcarbodiimide (DCC) were obtained from the Sinopharm Chemical Reagent (Shanghai, China). n-hexane and benzoyl peroxide (BPO) were purchased from Beijing Chemical Works (Beijing, China). Urea granules of 2–5 mm diameter were obtained from Heibei Cangzhou Dahua (Heibei, China). Other reagents were all obtained from the Sinopharm Chemical Reagent (Shanghai, China). All reagents were of analytical grade and used as received, except for BMA, MMA, and HEA, which were washed twice with 5% NaOH and twice with water, dried with CaCl$_2$, distilled over CaH under N$_2$, and stored at -4°C before use. The deionized water used in

all experiments was purified with a Milli-Q water system (Millipore, Milford, MO).

Synthesis of Polyesters of Poly(BMA–MMA–HEA)s with NAA (PBMHs-NAA)

Poly(BMA–MMA–HEA)s were synthesized first. Monomers of BMA, MMA, and HEA were added to a four-necked flask equipped with a N$_2$ inlet, a stirrer, a thermometer, and a condenser, and 0.45 wt % BPO vs. monomers dissolved in 5 mL of ethyl acetate (EA) was introduced, and the mixture was stirred at 85°C under N$_2$. A further 5 mL of 0.45 wt % BPO dissolved in EA was added after 2 h. If the mixture was too sticky to stir, an appropriate amount of EA was added to lower the viscosity of the mixture, and the total amount of EA vs. monomers was 2 : 1 (v/v). The mixture was allowed to react for another 4 h, and cooled. The unreacted monomers were removed by dissolving the product in EA and precipitating in n-hexane three times. Finally, the product was dried in an air oven overnight at 80°C. The poly(BMA–MMA–HEA)s with different ratios of monomers listed in Table I were prepared.

The poly(BMA–MMA–HEA)s were dissolved in EA, and NAA at the same molar ratio as HEA was added to the solution. The mixture was stirred in the presence of DCC and DMAP at room temperature for 12 h. The mixture was then filtered, and the filtrate was precipitated in n-hexane three times. The precipitates were dried in an air oven at 80°C. The amounts of pendant naphthylacetyl ester bound groups were determined from the ^{1}H NMR spectra. The PBMHs-NAA with different amounts of NAA were designated by P0, P1-NAA, P2-NAA, P3-NAA, and P4-NAA, referring to the HEA contents shown in Table I. The synthetic route to PBMHs-NAA is illustrated in Figure 1.

Characterizations

The PBMHs-NAA (0.5 g) was dissolved in 15 mL of EA, and the solution was cast on PTFE sheets (10 cm × 10 cm), and then dried at room temperature to obtain membranes of thickness about 0.1 mm for further characterizations.

FT-IR spectra were recorded in the range 500–4000 cm^{-1} with a resolution of 8 cm^{-1} on a Nicolet NEXUS-470 FT-IR spectrometer (Madison, NH). ^{1}H MNR spectra were recorded using tetramethylsilane (TMS) as an internal reference in CDCl$_3$ on a BRUKER DPX 300 MHz spectrometer (Bruker, Bremen, Germany) at ambient temperature. Thermal gravimetric analysis (TGA) was performed on a Q50 V20.6 Build 31 from TA Instruments (New Castle, DE) up to 600°C with a heating rate of 10°C min^{-1} under N$_2$, and the glass-transition temperature (T_g)
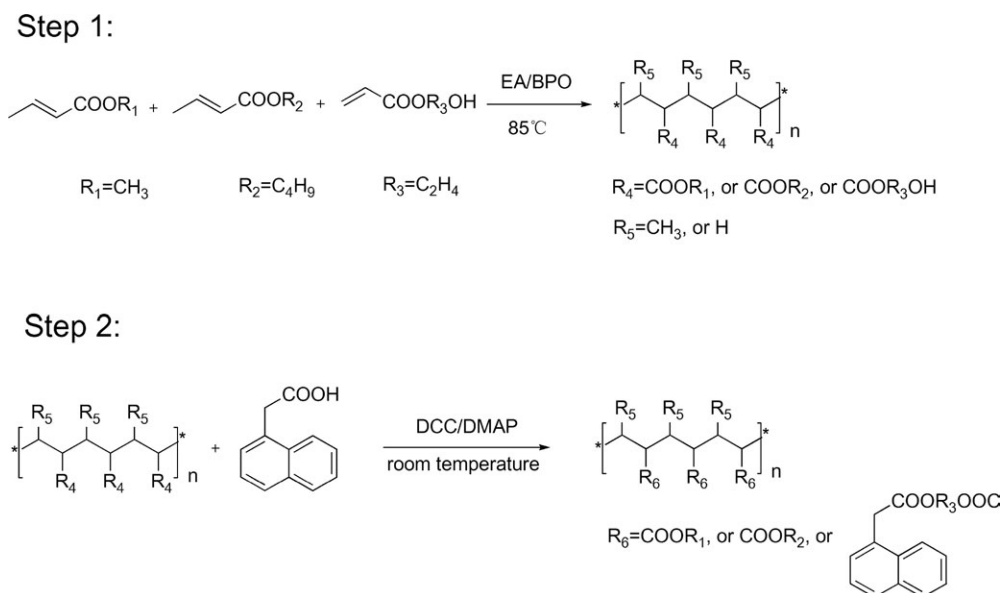
Figure 1. Synthetic route of PBMHs-NAA.

was determined using differential scanning calorimetry (DSC) on a Q100 V9.9 Build 303 from TA Instruments (New Castle, DE) under a N_2 flow from -20 to 150°C with a heating rate of 10°C min^{-1}. The membranes were cut into strips of size 7.5 mm × 1 mm for tensile strength measurements. Four tests were performed on each membrane, at room temperature, using an electronic universal testing machine CMT2102 (MTSChina, Shenzhen, China) at a stretching speed of 2 mm min^{-1}. Scanning electron microscopy (SEM) using a JEOL Instrument BACPCS4800 (Tokyo, Japan) at an accelerating voltage of 10 kV was conducted to investigate the surface and cross-section morphologies of the coated fertilizers.

Preparation of Coated Fertilizers and Measurements of Controlled-Release Properties

Urea granules (1 kg) were introduced in a fluidized bed, FLP3, from Changzhou Jiafa Granulating Drying Equipment (Changzhou, China), and preheated to 75°C with heated air introduced by a draught fan at 40 Hz. PBMHs-NAA (63 g) and paraffin (7 g) were dissolved in 1000 mL EA, and the solution was pumped into the bed using a peristaltic pump with a feed rate of 12 mL min^{-1}, and atomized using a spray nozzle under an air pressure of 0.15 MPa with an air compressor. After addition of the polyesters, the coating process was allowed to continue for 25 min and the fluidized bed was cooled to obtain the products. The coating rates were calculated as the weights of the coatings to the weights of the coated fertilizers.

The controlled-release properties of the coated fertilizers prepared were evaluated. The fertilizers (10 g) were immersed in 200 mL of distilled water in a plastic bottle incubated at 25°C. The solution in the plastic bottles was removed after a certain interval, and replaced by another 200 mL of distilled water. The urea content was determined by UV spectrophotometry, as in our previous work.[24] Three duplicates were conducted for each sample.

NAA Release from PBMHs-NAA

The impacts of pH, temperature, and NAA contents on NAA release from PBMHs-NAA were studied. The release experi-

ments were carried out in fresh buffer solutions at pH 4.2 (0.05 M NaOH, 0.2888 M CH$_3$COOH), pH 7.1 (water), and pH 9.0 (0.147 M NaHCO$_3$, 0.0178 M Na$_2$CO$_3$) at 25°C, and at temperatures of 20, 40, and 60°C in water (pH 7.1), using P4-NAA as an example. NAA release experiments from PBMHs-NAA with different contents of NAA (P1-NAA to P4-NAA) were conducted in water at 60°C. Typically, 0.3 g of PBMHs-NAA membranes was bathed in 100 mL of buffer solution in a beaker. At regular intervals, 10 mL solution was withdrawn and 10 mL of fresh buffer was added. The NAA content was determined by UV spectrophotometry at a wavelength of 283.5 nm.[17]

The PBMHs-NAA membranes were buried in sandy loam located at the Shangzhuang experimental station of the China Agricultural University (Beijing, China) to evaluate NAA release in a real environment. The physicochemical properties of the soil were described in an earlier publication.[25] The membranes were removed at regular intervals for analysis of NAA release rate using ^{1}H NMR.

Experimental Design and Statistical Analysis

Synthesis of the materials was conducted with five levels of HEA and NAA. Mechanical measurements were replicated four times for each sample. The release properties of the coated fertilizers and NAA were conducted with three replicates. The ^{1}H NMR data were analyzed using Mnova 6.1.1 software (Mestrelab Research, Escondido, CA). All the other data were analyzed using OriginLab scientific graphing and statistical analysis software (OriginLab, Northampton, MA). The statistical significance of differences in means was determined using the least-significant difference method at $P < 0.05$.

RESULTS AND NOTES

Structural Characterizations

The PBMHs-NAA were synthesized via the route as shown in Figure 1, and their structures were validated using both FT-IR (Figure 2) and ^{1}H NMR (Table I and Figure 3). The FT-IR
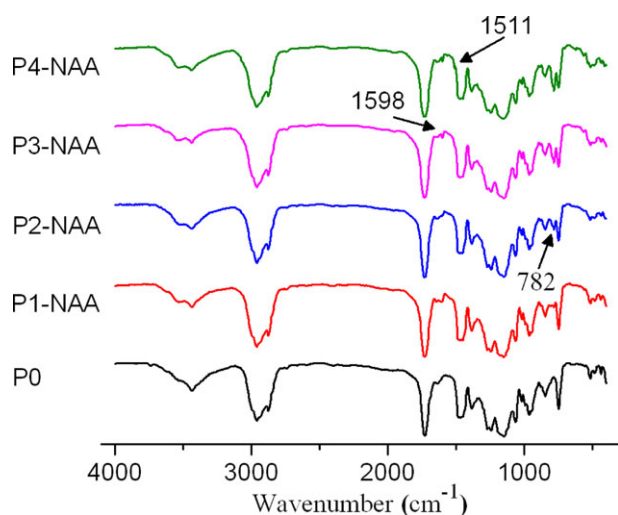
Figure 2. FT-IR spectra of PBMHs-NAA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

characteristic peaks of poly(BMA–MMA–HEA)s (Figure 2, P0) were C—H (CH$_3$ and CH$_2$) at 2960 and 2875 cm^{-1}, the stretching vibration of C—O at 1730 cm^{-1}, the stretching vibration of

O—H at 3440 cm^{-1}, and the strong characteristic absorption peaks of MMA and BMA at 1468, 1383, and 960 cm^{-1}, which were in accordance with earlier work.[26,27] The characteristic peaks at 782, 1511, and 1598 cm^{-1}, assigned to the vibrations of C—H and C=C in the naphthyl ring,[27,28] gradually strengthened as the NAA content increased (Figure 3, P1-NAA to P4-NAA).

The ^{1}H NMR characteristic peaks of PBMHs-NAA are shown in Table II and Figure 3. The NMR spectra of P1-NAA, P2-NAA, P3-NAA, and P4-NAA showed additional signals at 4.1 ppm derived from the methylene bridge of NAA and signals at 7.4–8.1 ppm, confirming the presence of naphthalene aromatic rings,[11,27,28] and the signals strengthened with increasing NAA content, with the absolute values of the integrals in the range 7.4–8.1 ppm increasing from 0 to 8073.05 (Table III, Figure 3). The combined FT-IR and ^{1}H NMR results indicated that NAA was successfully grafted onto the backbones of poly(BMA–MMA–HEA)s and the amount of grafted NAA could be regulated.

Thermal Properties

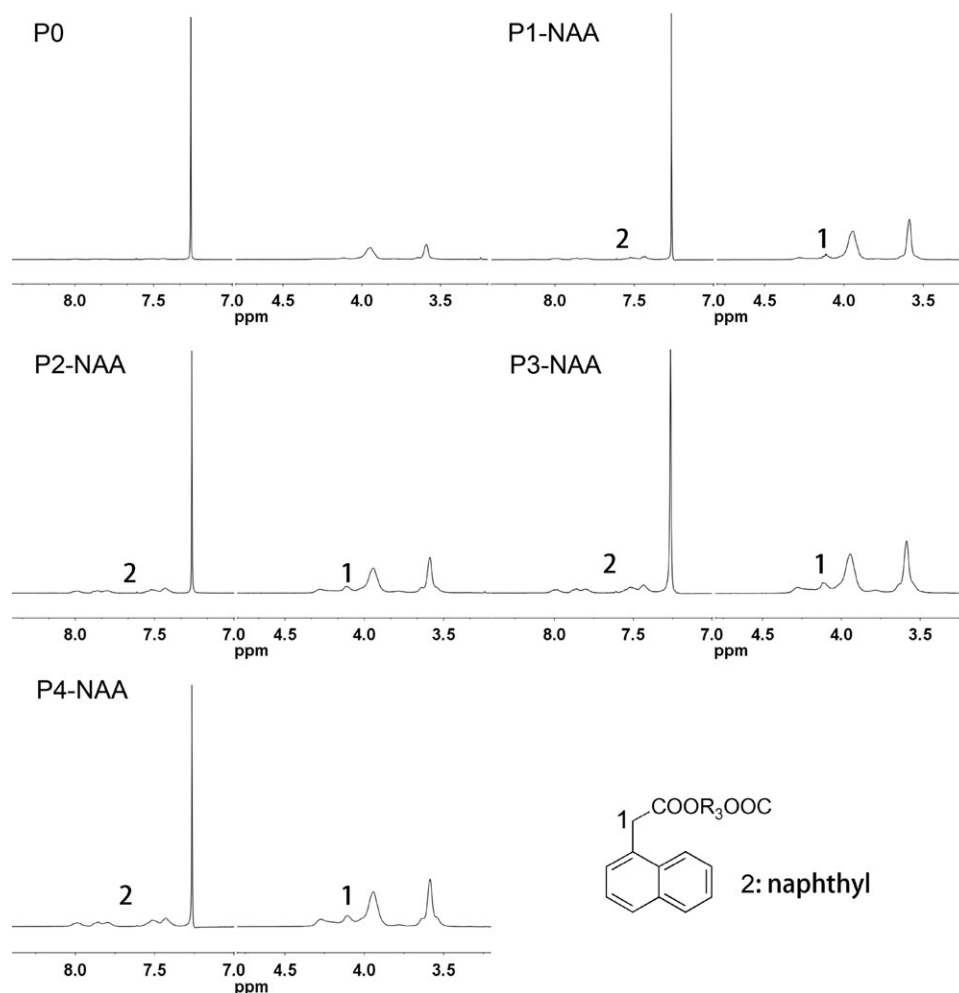Thermal decomposition behaviors and T_g values of the PBMHs-NAA were investigated by TGA and DSC, and the results are

Figure 3. ^{1}H NMR spectra of PBMHs-NAA in CDCl$_3$ at 300 MHz in the range 3.2–8.4 ppm.

Table II. ^{1}H NMR of PBMHs-NAA

Sample	^{1}H NMR (300 MHz, CDCl$_3$) δ (ppm)[a]
P0	–
P1-NAA	7.99 (s, 7, —C$_{10}$H$_7$), 7.87 (s, 7, —C$_{10}$H$_7$), 7.80 (s, 7, —C$_{10}$H$_7$), 7.52 (s, 7, —C$_{10}$H$_7$), 7.43 (s, 7, —C$_{10}$H$_7$), 4.12 (m, 2, —CO—CH$_2$—C$_{10}$H$_7$)
P2-NAA	7.99 (s, 7, —C$_{10}$H$_7$), 7.86 (s, 7, —C$_{10}$H$_7$), 7.79 (s, 7, —C$_{10}$H$_7$), 7.51 (s, 7, —C$_{10}$H$_7$), 7.43 (s, 7, —C$_{10}$H$_7$), 4.12 (s, 2, —CO—CH$_2$—C$_{10}$H$_7$)
P3-NAA	7.99 (s, 7, —C$_{10}$H$_7$), 7.86 (s, 7, —C$_{10}$H$_7$), 7.79 (s, 7, —C$_{10}$H$_7$), 7.52 (s, 7, —C$_{10}$H$_7$), 7.43 (s, 7, —C$_{10}$H$_7$), 4.12 (s, 2, —CO—CH$_2$—C$_{10}$H$_7$)
P4-NAA	7.99 (s, 7, —C$_{10}$H$_7$), 7.86 (s, 7, —C$_{10}$H$_7$), 7.79 (s, 7, —C$_{10}$H$_7$), 7.51 (s, 7, —C$_{10}$H$_7$), 7.43 (s, 7, —C$_{10}$H$_7$), 4.12 (m, 2, —CO—CH$_2$—C$_{10}$H$_7$)

[a]Peaks which are not related to naphthylacetic ester groups are not listed.

Table III. Absolute Values of Integrals in the Range 7.4–8.1 ppm at Different Times Calculated from ^{1}H NMR Spectra

Sample	Initial	6 months after burying	12 months after burying
P0	0	0	0
P1-NAA	3877.60	1670.09	1214.80
P2-NAA	4103.89	3269.35	1510.63
P3-NAA	5538.34	4841.27	4716.63
P4-NAA	8073.05	7151.95	6115.27

shown in Figure 4. The weight-loss behavior with respect to the water probably bound to the PBMHs-NAA was observed in the range 100–250°C. The second degradation stage of the polymers was in the range 250–300°C, and the third was in the range 300–430°C, which were in accordance with the typical decomposition behaviors of polyacrylates.[29–31] The second stage was related to the decomposition of the head-to-head linkages, and the third was related to the unzipping of the polymers via random scission of the polymer chains.[31] The decompositions of the PBMHs-NAA shifted to higher temperatures compared to that of P0, and higher temperatures were needed to degrade polymers with higher contents of NAA, indicating that grafting NAA improved the thermal stability of the polymers.

The T_g values of the PBMHs-NAA had a great influence on the coating process of the fertilizers, because the polymer became sticky at coating temperatures higher than the T_g and the coatings were imperfect, leading to uncontrolled release of nutrients. The T_g values of the PBMHs-NAA were calculated from the DSC curves (Figure 3, right), and decreased from 53.9°C for P0 to 40.0°C for P4-NAA. The decrease in T_g was probably caused by the decrease in BMA and increase in HEA in the copolymer backbones.[32,33]

Mechanical Properties

The applicability of PBMHs-NAA for coating fertilizers depends on the mechanical properties, which are of vital importance for transportation of fertilizers. From Figure 5, it can be seen that the tensile strength and Young's modulus increased from 19.28 MPa and 1.27 GPa to 29.32 MPa and 1.77 GPa, respectively, with increasing NAA content, whereas the elongation at break decreased from 3.11 to 2.34%. These results demonstrated that the PBMHs-NAA became stiffer and more brittle as the NAA content increased, and this was probably a result of the increase in HEA in the backbones of the copolymers; similar results were obtained in a previous work.[34] The stiffness and brittleness of PBMHs-NAA are not applicable to coating fertilizers, so for practical applications the content of NAA grafted on the polymer could not be too high.

Properties of Coated Fertilizers

P0 and P2-NAA were selected for coating fertilizers. The release properties of the coated fertilizers are shown in Figure 6, and the morphologies of the coated fertilizers are shown in Figure 7.
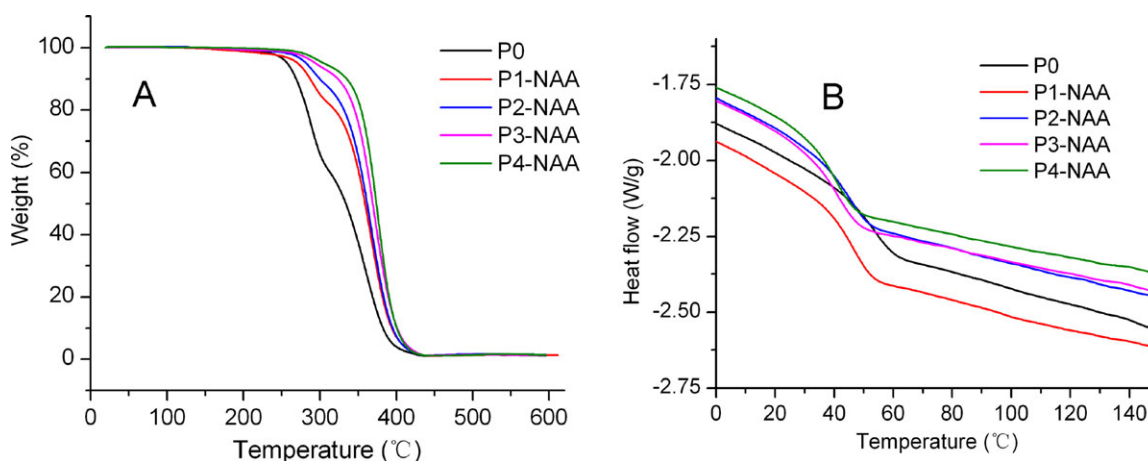

Figure 4. TGA curves (A) and DSC curves (B) of PBMHs-NAA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
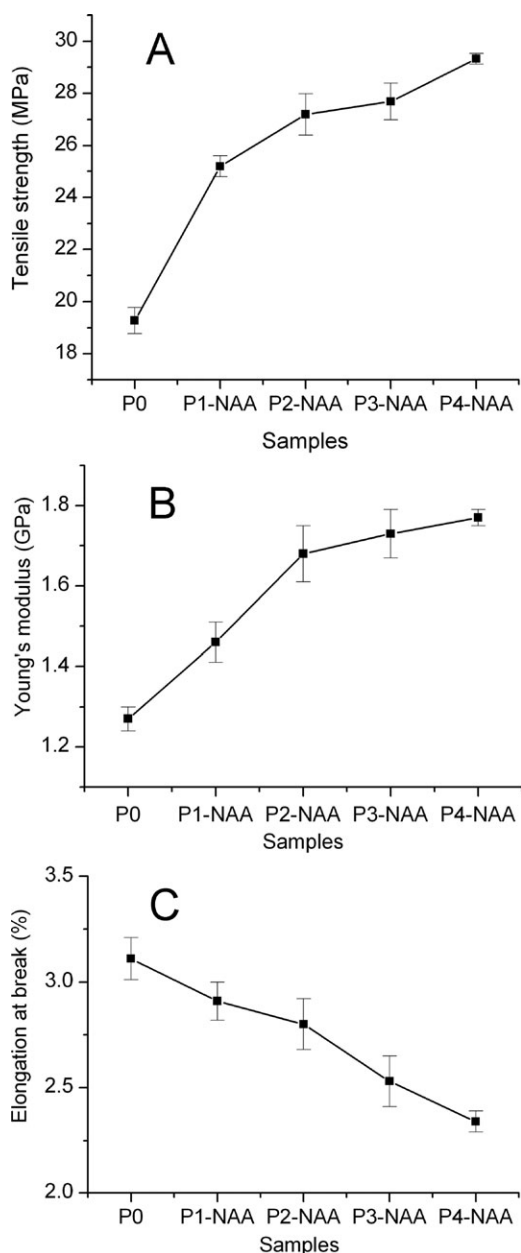
Figure 5. Mechanical properties of PBMHs-NAA. A: tensile strength; B: Young's modulus; and C: elongation at break.

From Figure 6, it can be observed that for P0 and P2-NAA, the urea released rapidly and the durations were all about 8 days. The main reason was the sticky adhesion between the coated granules particles damaging the uniformity of the coated layer. However, after 10% of paraffin was added into the coating solution, the release property of the coated urea enhanced significantly. And the super hydrophobicity of paraffin incorporated in the coating layer improved the isolation between urea and water. It can be found that 0.78 and 1.54% of nutrients were released from the fertilizers coated with P0 and P2-NAA in the first 24 h, respectively, and after 28 days of incubation, 70.68 and 78.77% were released. In the first 7 days, the release rates were relatively low, but became higher after that. These proper-

ties made the coated fertilizers fully meet the descriptions of European Committee for Standardization (EN 13266:2001) and Chinese standard GB/T 23348-2009. It was obviously that the addition of paraffin in the coating solution could greatly reduce the sticky strength of the polymer granules during the coating process. The P0 and P2-NAA coatings were both intact and adhered tightly to the core, and the thicknesses were around 45 μm (Figure 7). It was also observed that the P2-NAA coating was slightly more compact and uniform than the P0 coating, which was why fertilizer coated with P2-NAA was better than that coated with P0. In the coating process, molecules of polymers with lower T_g values migrated more easily, thus more compact and uniform coatings formed. These results demonstrated that the PBMHs-NAA were suitable for coating fertilizers and that the coated fertilizers possessed controlled-release properties.

Release Properties of NAA

As a result of hydrolysis of ester bonds of NAA linked to the copolymers, NAA was released from PBMHs-NAA. The release properties of NAA are shown in Figure 8. The hydrolysis of all the PBMHs-NAA followed first-order kinetics ($R^2 = 0.876$–0.992), which was consistent with earlier studies.[11,12] The hydrolysis rate constant at pH 9.0 was 0.308 mg days^{-1}, calculated from the slope of a plot of the mass of NAA released against time, compared to 0.160 mg days^{-1} at pH 4.2 and 0.144 mg days^{-1} at pH 7.1 [Figure 8(A)]. The hydrolysis rate at alkaline pH values was much higher than that at acidic pH values, simply because of the greater availability of OH$^-$, which could neutralize the released NAA and promote hydrolysis.[8,11,12] This result also demonstrated that hydrolysis rate of PBMHs-NAA was higher in acidic condition than in neutral condition, and this was verified in other publication.[8] Figure 7(B) shows that temperature had great influence on the hydrolysis rates, increasing from 0.042 mg days^{-1} at 20 °C to 0.507 mg days^{-1} at 60°C. It was previously found that hydrolysis at room temperature and in the pH range 4–7 was negligible,[8] and this was confirmed by the results of hydrolysis at 20°C, pH 7.1 [Figure
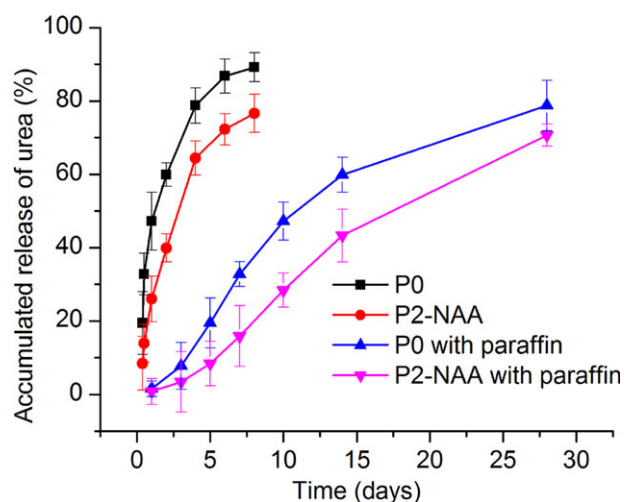

Figure 6. Accumulated release of urea from coated fertilizers in water (25°C). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
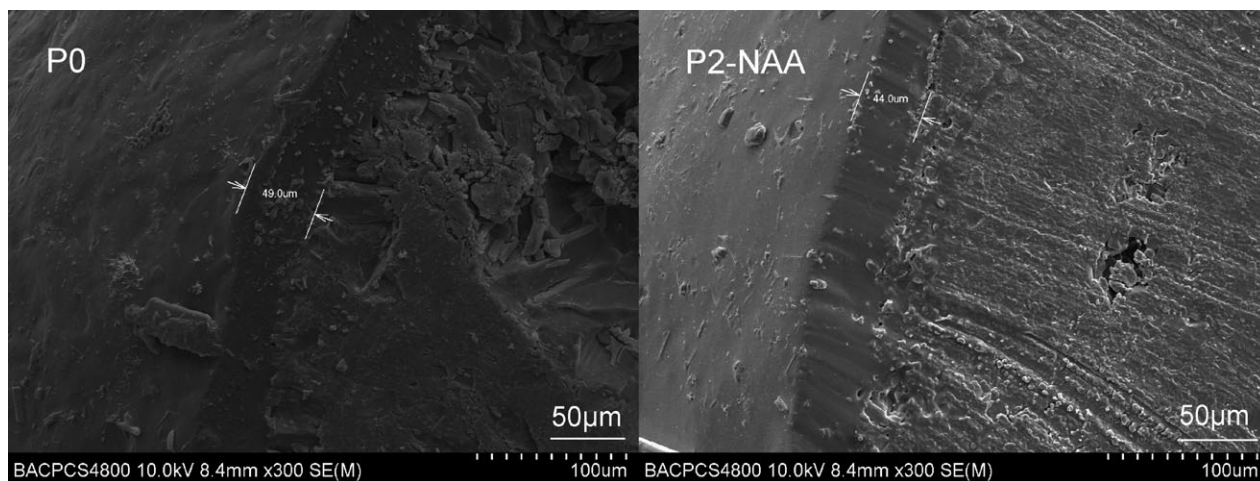
Figure 7. SEM images of fertilizers coated with P0 (left) and P2-NAA (right).

7(B)]. Higher temperatures provided higher energies for bond dissociation and thus facilitated the hydrolysis of PBMHs-NAA.[35] The hydrolysis rate constants increased from 0.094 mg days^{-1} for P1-NAA to 0.341 mg days^{-1} for P4-NAA with increasing NAA content, which indicated that the NAA content did not influence the hydrolysis of PBMHs-NAA; higher NAA
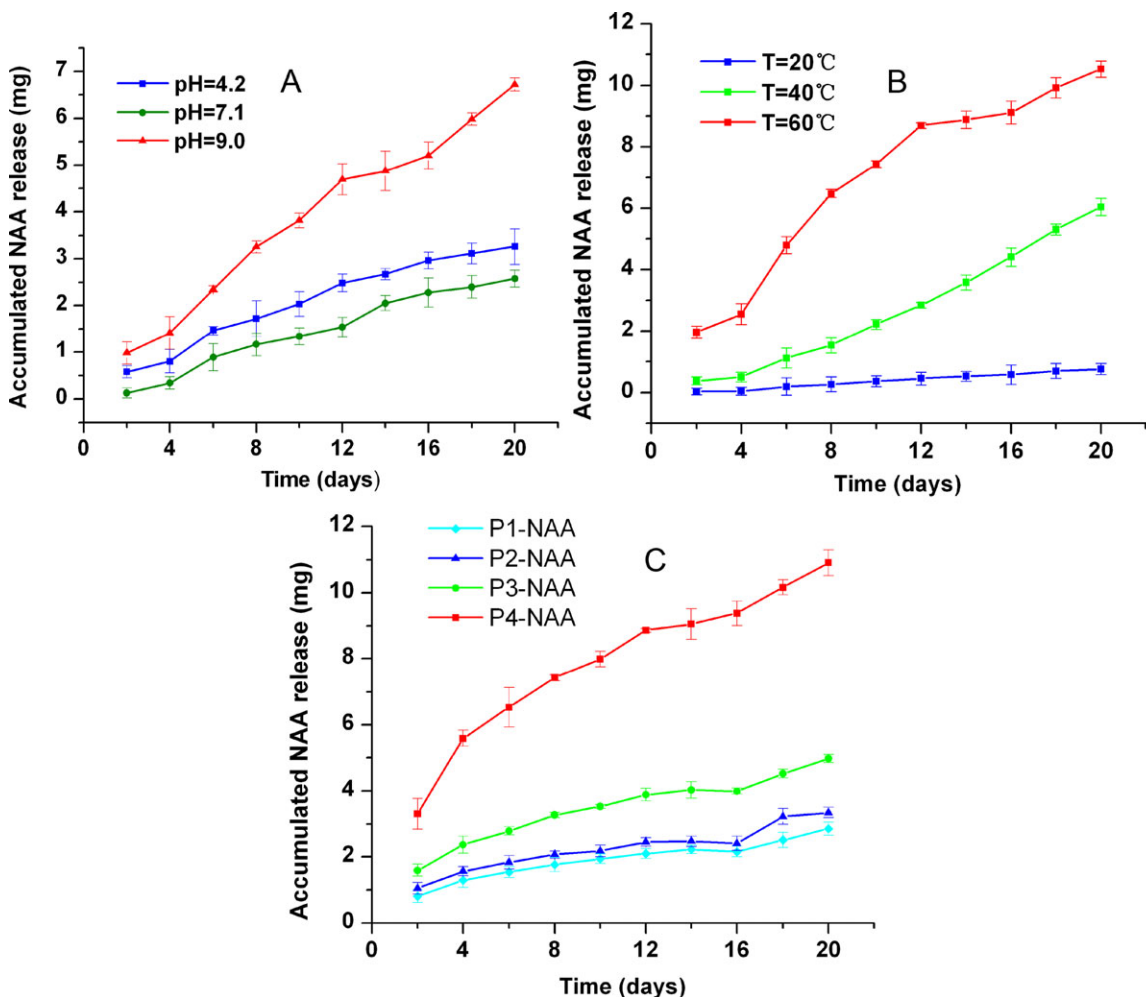

Figure 8. Parameters influencing the accumulated release of NAA from PBMHs-NAA in buffer solutions. A: pH, sample: P4-NAA, 25°C; B: temperature, sample: P4-NAA, pH 7.1; C: contents of NAA, pH 7.1, 60°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
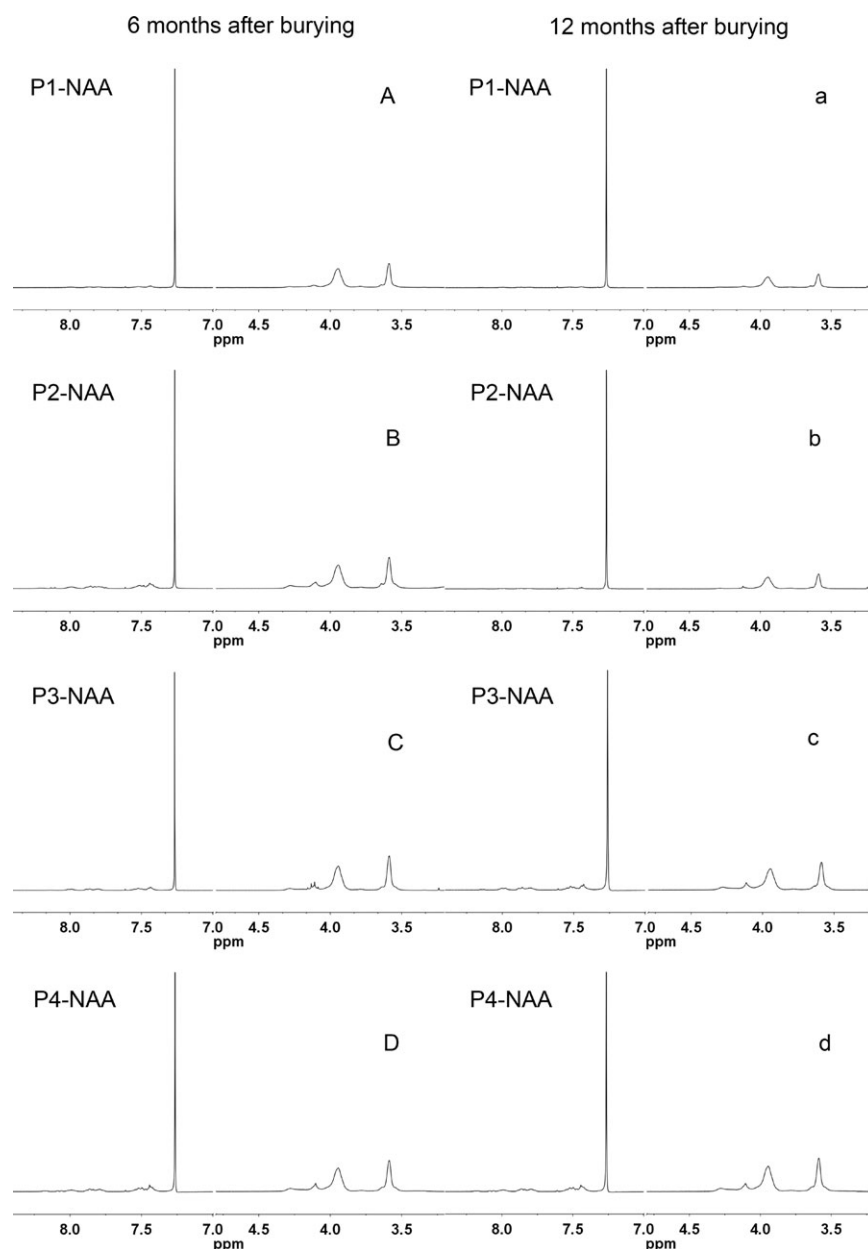
Figure 9. ^{1}H NMR spectra of PBMHs-NAA in CDCl$_3$ at 300 MHz in the range 3.2–8.4 ppm, after burial in soil for: A–D: 6 months; a–d: 12 months.

contents led to increased NAA release. In other studies, in which NAA was combined with hydrophilic polymers, the hydrolysis rate decreased with increasing NAA contents,[8,11] but the poly(BMA-MMA-HEA)s and NAA esters in this study were hydrophobic, thus grafting of NAA did not change the hydrophobicity of the copolymers, and consequently the hydrolysis did not change in the reverse direction with NAA content.

Enzyme hydrolysis of NAA esters also takes place at reasonable rates in soils.[8,36] The PBMHs-NAA membranes buried in soil were removed after 6 and 12 months, and they were analyzed using ^{1}H NMR (Figure 9). Table III shows the absolute values of integrals in the range 7.4–8.1 ppm of the spectra, from which it was calculated that 11.4–56.9% and 14.8–68.7% of NAA were released from the polymers after burial in soil for 6 and 12

months, respectively. NAA release from the polymers presented a general decreasing trend with increasing NAA content, but the mechanism is not clear yet. The residual amounts of NAA in the PBMHs-NAA were 31.3–85.2% after burial in soil for 12 months, indicating that the polymers could release NAA to the soil for even longer time, and this result was confirmed by inhibition of sucker growth of grapevines after application of NAA esters.[10] These results demonstrated that the PBMHs-NAA could regulate the release of NAA, thus providing controlled-release properties of NAA for various applications.

CONCLUSIONS

NAA functioned polyacrylate for coated urea was successfully prepared. The thermal and mechanical properties of the

PBMHs-NAA were characterized, illustrating that the polymer was suitable for coated fertilizers. The release behavior of the coated urea was conducted in water and urea was sustainably released for more than 28 days. The hydrolysis of NAA from the PBMHs-NAA was preceded both in buffer solutions and natural soil. The temperature and pH had great influences on the release rates of NAA in buffer solutions. The release of NAA of the polymer membranes could last for more than 12 months in soil from the results of ^{1}H NMR. The urea coated with poly-acrylate with pendant NAA side groups had the typical features of dual controlled-release of urea and NAA, and the coated fertilizers had great potential in agriculture for sustained-release of plant nutrients and PGRs.

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