J Mater Sci
DOI 10.1007/s10853-016-9775-0

Formulation and characterization of polysaccharide beads for controlled release of plant growth regulators

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Received: 12 November 2015 / Accepted: 22 January 2016

Abstract Owing to their chemical, physical, and functional characteristics, polysaccharides are considered to be the most versatile natural polymers. As a result, their properties have been exploited in various fields of research in the biomedical, pharmaceutical, cosmetic, food, and agricultural industries. A property of special interest is their ability to form systems or materials with unique physicochemical characteristics, such as hydrogels and micro- and nanoparticles for controlled release of active compounds. In the present study, polysaccharide beads formulated from alginate, cellulose powder, cellulose nanocrystals, starch, and xylan were reinforced with kaolin and surface-modified with polyethylenimine (PEI), a positively charged polyelectrolyte. Addition of kaolin improved the mechanical strength of the beads. Modification of the surface of the beads with PEI facilitated better control of the release rate of the plant growth regulator, phenylacetic acid (PAA). The physical properties of the beads were characterized by optical and scanning electron microscopy, and their mechanical strength was determined by an Instron 5565 Tensile Testing Machine. Cumulative release of PAA was measured by UV–Vis spectroscopy.

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Introduction

Agrochemicals, such as pesticides, herbicides, fertilizers, and plant hormones, improve the production of crops and play an important role in maintaining the increasing demand of food for a growing global population. While conventional agrochemical formulations are using a greater amount of chemicals over a longer period of time than is actually needed, the harmful effect of these chemicals of causing crop damage, environmental pollution, and health risks is the real major limitation of their application [1–3]. Evaluating and balancing beneficial and adverse effects of agrochemicals can be problematic [4]. Hence, safely handling of these chemicals is essential and appropriate application systems, aiming at lower dosage and site-specific release at a slower and more controlled rate over a prolonged period of time, must be found [5, 6]. Controlled release systems can optimize the applicable efficiency of bioactive chemicals and minimize the residues of agrochemicals [2]; thus, a feasible approach to reduce efficiency loss, pollution, and health risks due to leaching, volatilization, and biodegradation needs to be developed.

In recent years, a great deal of interest has been focused on exploring low-cost, biodegradable, and non-toxic materials as reservoirs/carriers for improved controlled discharge of agrochemicals [7, 8]. Polysaccharides are among the most promising candidates of all renewable compounds for this purpose [6, 9, 10] and play an important role, especially in the form of hydrogels [2, 11–15] and beads [16–24]. They are capable of slowly releasing agrochemicals and simultaneously increasing the water-holding capacity of soil [25]. In addition, polysaccharides can also serve as nutrients in the field after degradation by soil microorganisms. Alginic acid is an anionic naturally abundant polysaccharide extracted from brown seaweed

Published online: 03 February 2016

and soil bacteria. Chemically, it is a linear copolymer composed of two monomers, (1-4)-linked β-D-mannuronic acid (M) and α-L-glucuronic acid (G) residues of different ratios and distribution along the chains [26]. In aqueous solution at neutral pH, alginate contains a significant amount of negative charges due to deprotonated carboxylic acid groups. These negative charges enable alginate to induce repulsive electrostatic forces and to swell as well as to interact with positively charged ionic groups. Alginate exhibits a sol–gel transition by forming the so-called "egg-box" structure when sodium counter-ions are substituted with divalent cations, such as calcium, zinc, or barium [26].

Beads made from crosslinked sodium alginate have been found to be suitable as a supporting matrix for controlled release of agrochemicals as documented in numerous publications. For instance, pesticide/herbicide/plant growth regulator loaded sodium alginate beads were crosslinked with glutaraldehyde [20] and various divalent metal ions, e.g., calcium [18, 19, 21–23] and nickel [18]. Various clays such as kaolin have been used as additives in polysaccharide based controlled release systems to further reduce the release rate [21, 22]. It was found that the composition of the beads and the type of crosslinking agent (cation type and concentration), as well as other factors, such as crosslinking time, surface coating, and pH of the release media also affected the release kinetics.

Moreover, neutral and anionic polysaccharide fillers such as starch, cellulose, and xylan have potential to improve the alginate bead system by influencing the release rate of the targeted agrochemicals. However, to our knowledge, a comparative study of different combinations of polysaccharide and kaolin fillers in combination with a surface coating has not yet been performed. The work described in this paper is concerned with polysaccharide–kaolin blended beads without/with polyethylenimine surface coating. The beads before coating are composed of alginate, kaolin, and an additional polysaccharide as the filler (starch, cellulose powder, cellulose nanocrystals (CNC), and xylan). Both the bead components and the cationic coating were designed to influence the internal and external properties of beads and to optimize the controlled release of phenylacetic acid (PAA). The average size and size distribution of dry beads, their swelling ratios, mechanical strength under compression, and their morphologies were studied. In addition, the cumulative release of PAA, an anionic plant growth regulator, was assessed. The application of the cationic polyelectrolyte polyethylenimine (PEI) after the beads were crosslinked with calcium ions was intended to reduce the release rate of PAA by forming an extra electrostatic barrier to the free passage of PAA. It was found that the cumulative release was clearly affected by the composition of the beads and the PEI coating. The admixture of the polysaccharide filler proved to be a key factor affecting morphology, while the PEI coating influenced the swelling ratio, compressive strength, and cumulative release of PAA.

Experimental

Materials

Alginic acid sodium salt (medium viscosity), cellulose (powder, ~20 micron), xylan from beech wood, and polyethylenimine (branched, PEI) were purchased from Sigma-Aldrich. Cellulose nanocrystals (CNC) were provided by the U.S. Department of Agriculture, Forest Products Laboratory, Madison, WI. Phenylacetic acid (PAA) was purchased from Alfa Aesar and kaolin was from Ward's Science. Corn starch was food grade, and calcium chloride was purchased from Merck. All materials were used as received.

Preparation of beads

Various combinations of aqueous suspensions carrying 0.03 M PAA were prepared by mixing 2 % w/v sodium alginate, 2 % kaolin w/v with 1 % w/v corn starch, cellulose powder, xylan or CNC, respectively, with deionized water. All suspensions were mixed homogenously using a magnetic stirrer at 1000 rpm at room temperature for 3 h. The suspensions were added dropwise to 0.2 M aqueous calcium chloride solution as the crosslinking agent through a 10-mL syringe with a needle size of 18G × $1^1/_2$. The syringe was pushed by a syringe pump at a constant rate of 4 mL/min. The beads were left in calcium chloride solution to harden for 30 min with gentle stirring. Finally, they were washed three times with deionized water to remove the calcium chloride left on the surface. A portion of freshly made beads were air dried for 48 h; a second batch was further crosslinked with 2 % and a third batch with 4 % w/v PEI aqueous solution for 2 h. The beads were washed with deionized water and air dried for 48 h.

Size measurement of beads

Optical microscopy was used to measure the size of air-dried beads. 20 beads within each sample and three diameters for each bead (maximum, minimum and diagonal) were measured, and the average diameter was calculated and recorded.

Swelling ratios of beads

The weight of the dried beads and beads immersed in deionized water for 48 h at room temperature were determined. The swelling ratio was evaluated using Eq. 1:

$$\text{Swelling ratio } \% = \frac{W_s - W_d}{W_d} \times 100\ \%\ , \quad (1)$$

where W_s is the weight of the water-swollen beads and W_d is the weight of the dried beads.

Mechanical strength measurements

10 beads of each composition were compressed individually by an Instron 5565 Tensile Testing, with the compressive force increasing from 0 to 10 kg at a rate of 10 kg/min. The compressive force and deformation of each bead were recorded. After the test, the force that caused 30 % bead deformation was averaged and plotted in relationship to the bead composition.

Scanning electron microscopic (SEM) and energy-dispersive spectroscopy (EDS) analysis of beads

The surface morphology of dried beads before and after the compression test as well as morphology of bead cross sections before compression were observed by scanning electron microscopy (SEM) at a 20 kV accelerating voltage and working distance 5.5–9 mm, using a Zeiss EVO 50 Variable Pressure SEM. The samples were sputter coated with gold in an EMS 550X Auto Sputter Coating Device.

Weight percentage of calcium and other elements on the beads' surface and at the interior cross sections was measured by energy-dispersive spectroscopy (Inca EDS system) connected with SEM at a 20 kV accelerating voltage and working distance of 9 mm. The samples were sputter coated with carbon in an EMS 550X Auto Sputter Coating Device.

Cumulative release of PAA into water

One g of beads was placed into a beaker with 100 mL deionized water and stirred at 100 rpm for 48 h. Three mL of solution was measured by UV–Vis spectroscopy every 30 min during the first 4 h and then at 5, 6, 24 and 48 h. After each measurement, three mL of fresh deionized water was added to the beaker to keep the volume of the solution constant at 100 mL. The measurement procedure for one sample was repeated three times. The cumulative release (%) was calculated according to Eq. 2:

$$\text{Cumulative release}(\%) = 100\,\% \times (C_i V + C_{i-1}R + C_{i-2}R + \cdots + C_{i-n}R)/W, \quad (2)$$

where i is the number of measurement, C_i is the concentration of PAA in the solution at ith measurement, V is the total volume of release solution, R is the volume of fresh medium, and W is the total weight of PAA entrapped in the beads before the release.

Results and discussion

Size and size distribution analysis

Average diameter and standard deviation of beads dried at room temperature were plotted, and the results are displayed in Fig. 1. Beads crosslinked only in 0.2 M $CaCl_2$ solution are marked as "series 1"; those coated with 2 % PEI and 4 % PEI, respectively, are designated "series 2" and "series 3," respectively. Beads composed of 2 % alginate and 2 % kaolin constituted the control sample. All other beads contained 1 % of an additional polysaccharide filler based on the control sample.

Beads made of different components within the same series showed small differences in average diameter. The concentration of alginate and the polysaccharide filler was always kept at a ratio of 2:1 (w/w). The size of the filler polysaccharide and the interaction of filler molecules with the alginate bead (e.g., repulsion between different functional groups, crosslink density) may have influenced the actual observed size of the beads. For instance, beads containing xylan showed the second largest size among all samples without PEI coating. This may be attributed to the additional negatively charged carboxylic acid group allowing more Ca^{2+} to combine within the alginate bead. Thus, it is likely that beads containing xylan formed a

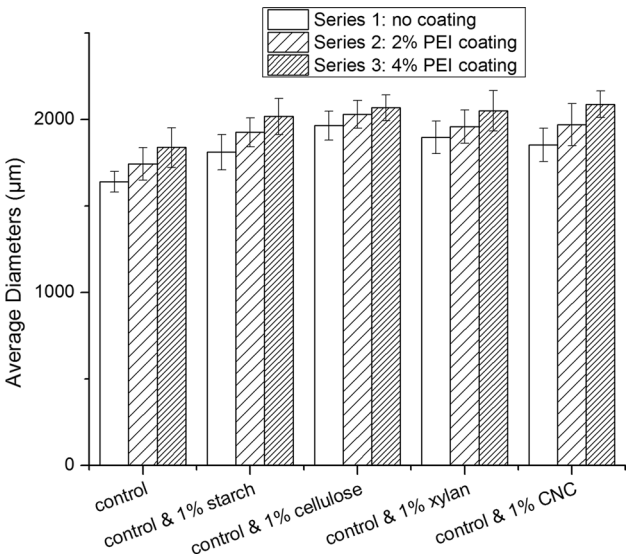

Fig. 1 Average diameters of beads; series 1: beads with no coating, series 2: beads with 2 % PEI coating, and series 3: beads with 4 % PEI coating

stronger electrostatic interaction to support the bead structure during drying.

Since the PEI was branched and had a high molecular weight ($M_n \sim 10{,}000$), it was not expected to penetrate the beads' surface structure but only form a coating on the exterior of the beads. This assumption was confirmed scanning electron microscopy.

As can be seen from Fig. 1 and Table 1, beads of comparable composition were slightly larger (3–5 %) when coated with 2 % PEI aqueous solution. At 4 % PEI concentration, the bead' sizes increased by 6–11 % compared to the uncoated samples. In contrast to the bead size, the weight increase of the beads after coating was much larger than the size increase especially with 4 % PEI (aq). This may indicate that PEI as a positive-charged polyelectrolyte created additional electrostatic interactions with additional negative charges from COO^- and may exchange Ca^{2+} from the previous Ca^{2+}–COO^- crosslink sites, resulting in beads with a firmer and denser structure at the outside layer. It was observed that the higher the concentration of PEI, the firmer and denser the bead surface. It can be hypothesized that the weight increase mostly contributed to the increase in surface layer density.

Swelling ratios

Table 2 shows the swelling ratios of beads without coating as well as with 2 and 4 % PEI coating. Beads without coating had rather similar swelling ratios. However, beads with PEI coating clearly showed higher swelling ratios. Even though it has been argued that beads with PEI coating are surrounded by a firmer surface layer, the layer itself may still contain highly branched PEI and thus be able to absorb liquids. Therefore, this may be the major factor contributing to the observed greater swelling ratio. Overall, beads containing xylan and CNC and coated with 2 and 4 % PEI solution showed the highest swelling, especially in the case of xylan. This may be the result of additional negative charges on xylan interacting with more amino groups on PEI. In previous work (unpublished data) on charge density of different polysaccharide combinations, alginate with xylan clearly had the highest negative charge density among all samples.

Table 1 Beads' weight increase (%) after coating with 2 %/4 % PEI (aq)

	2 % PEI	4 % PEI
Control	3.9 ± 0.08	15.1 ± 0.61
Control & 1 % starch	4.1 ± 0.11	16.3 ± 0.43
Control & 1 % cellulose	3.6 ± 0.18	14.8 ± 0.37
Control & 1 % xylan	5.4 ± 0.32	21.8 ± 0.64
Control & 1 % CNC	5.1 ± 0.27	19.6 ± 0.86

Mechanical strength analysis

Mechanical properties of three series of beads along with beads made of alginate alone were investigated. Beads made of alginate alone were compared with those reinforced with kaolin to investigate the effectiveness of kaolin in improving the mechanical strength of the alginate beads. The average compressive force causing 30 % deformation of each bead sample is shown in Fig. 2. Beads made from alginate alone proved to be the weakest. Beads within each

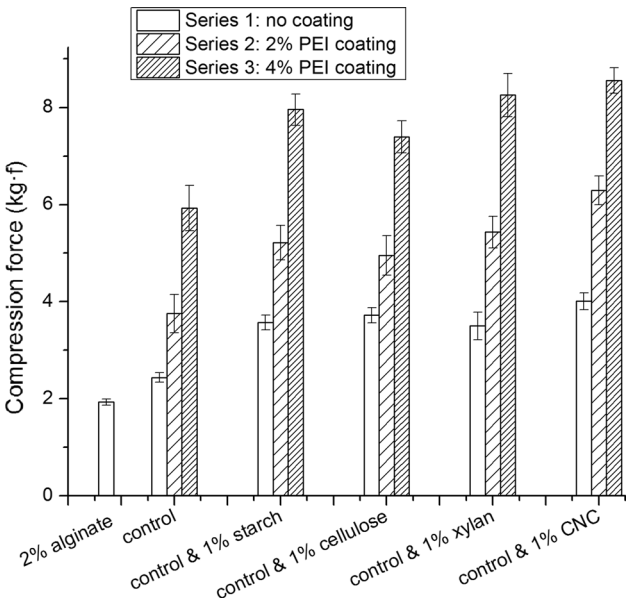

Fig. 2 Compression force applied to 30 % deformation of beads

Table 2 Swelling ratios data (%) of beads without/with coating

	No coating	2 % PEI	4 % PEI
Control	24.5 ± 0.87	34.1 ± 1.19	61.4 ± 1.02
Control & 1 % starch	26.7 ± 0.42	39.3 ± 0.81	78.1 ± 1.09
Control & 1 % cellulose	22.2 ± 0.59	32.1 ± 0.78	62.3 ± 1.28
Control & 1 % xylan	31.1 ± 0.82	46.8 ± 0.73	96.2 ± 1.16
Control & 1 % CNC	27.9 ± 0.53	41.7 ± 0.62	84.4 ± 1.91

series showed a slight difference, which likely indicated that the polysaccharide filler did not sufficiently enhance the mechanical strength of the bead. However, PEI coating indeed strengthened the bead structure and higher PEI coating resulted in higher mechanical strength overall. To be more specific, beads without coating reached 30 % deformation by a force of 2.5–4 kg. For beads coated in 4 % PEI solution, the compressive force increased to 6–8.5 kg. Some cracks appeared at the edges of the beads when the compressive force reached the maximum set in the experiment (10 kg) as could be demonstrated by SEM (see below, Fig. 6).

Morphology analysis and element composition

The surface morphologies of different beads without coating are shown in Fig. 3. The differences in appearance may be attributed to the physical form of the polysaccharide filler and the way the polysaccharide combinations were able to interact. The beads formed from alginate and kaolin alone had relatively smooth surfaces (Fig. 3a), while beads containing 1 % starch showed a more granular structure probably because the original granular structure from corn starch was still preserved (Fig. 3b). Blending alginate with 1 % cellulose powder created a coarser

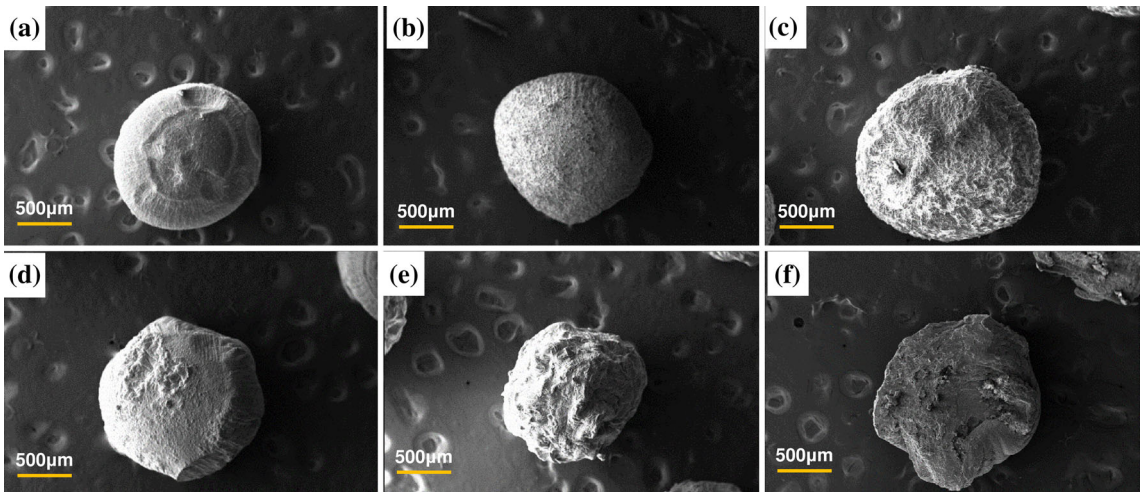

Fig. 3 Surface morphology of beads composed of **a** control, **b** control & 1 % starch, **c** control & 1 % cellulose, **d** control & 1 % xylan, **e** control & 1 % CNC, **f** cross section of control sample

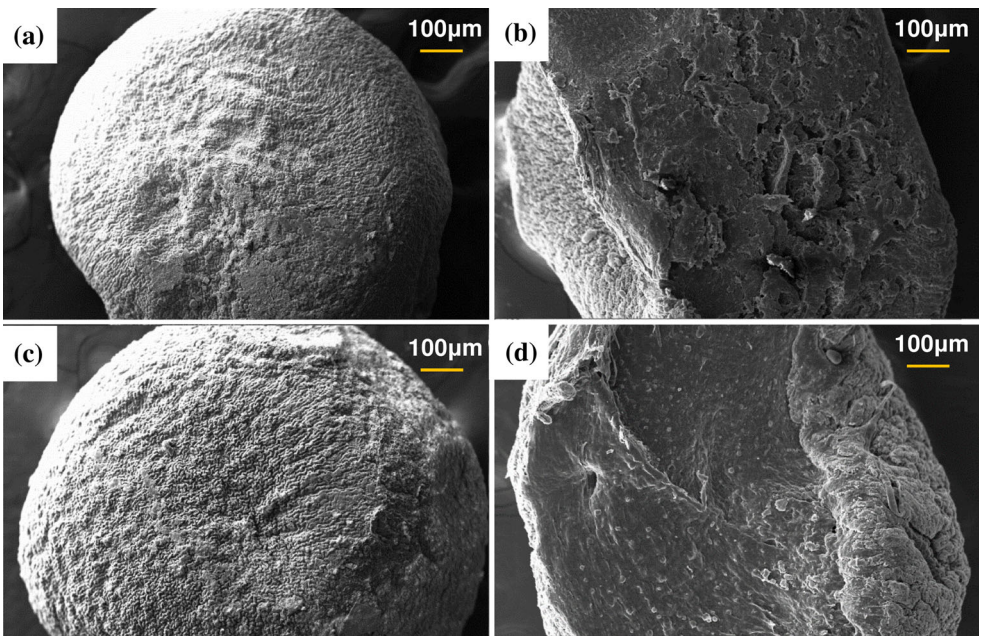

Fig. 4 Bead surface and cross section morphologies: control with 1 % xylan: 2 % PEI, 4 % PEI coating **a** and **c**; **b** cross section of **a**, **d** cross section of **c**

surface morphology of the resulting beads (Fig. 3c). The roughest surfaces were observed with CNC admixtures (Fig. 3e).

The cross sections of the beads did not differ significantly. Figure 3f depicts a cross section through a control bead, representative of all other beads. They all had a fairly compact structure with more or less equal sized pores and some cracks.

As can be seen in Fig. 4a, c, beads with xylan, as representative of all samples, adopted a rougher surface after coating in PEI solution. The more the coating was applied, the more rugged the surface tended to become. It can also be seen from Fig. 4b, d, the cross sections of cut beads with PEI coating were only rough on the outside the bead, not in the interior.

Table 3 Elements found on the surface and the interior of beads (control containing 1 % CNC) without and with 2 % PEI coating (wt%)

	No coating		2 % PEI	
Elements	Surface	Interior	Surface	Interior
Na	1.30	1.29	–	–
Al	19.56	20.94	29.45	28.51
Si	27.28	28.11	45.63	42.72
S	–	1.13	1.90	2.57
Cl	24.93	26.35	4.68	3.58
Ca	26.93	22.17	16.63	20.63
Ti	–	–	1.70	1.99
Total	100.00			

EDS in conjunction with SEM was used to determine the element composition of the surface of the beads in comparison to the interior at cross sections. Representative of all samples, data for beads with CNC with/without PEI coating are presented in Table 3 and Fig. 5. Generally, Ca and Cl were directly from crosslinking. A small amount of Na indicated that a minor portion of sodium alginate could not bind with calcium ions. Sulfur probably originated from sulfate groups on CNC which had been hydrolyzed by sulfuric acid, and Al, Si, and Ti came from kaolin. Carbon and oxygen are not reported as they exist in all samples and are distributed evenly within each sample.

As can be seen from Table 3 and Fig. 5a, b, beads without coating had a higher weight percentage of calcium on the surface compared to the central cross section. This might be due to the relatively short crosslinking time of 30 min and Ca^{2+} could not sufficiently reach all carboxylic groups in the center area of beads.

After coating in PEI solution, the content of calcium on the exterior of the beads was lower than that of the central cross-sectional area (Table 3; Fig. 5c, d; shown for 2 % PEI). Overall the concentration of PEI did not play a major role as coating in 2 and 4 % solution yielded very similar

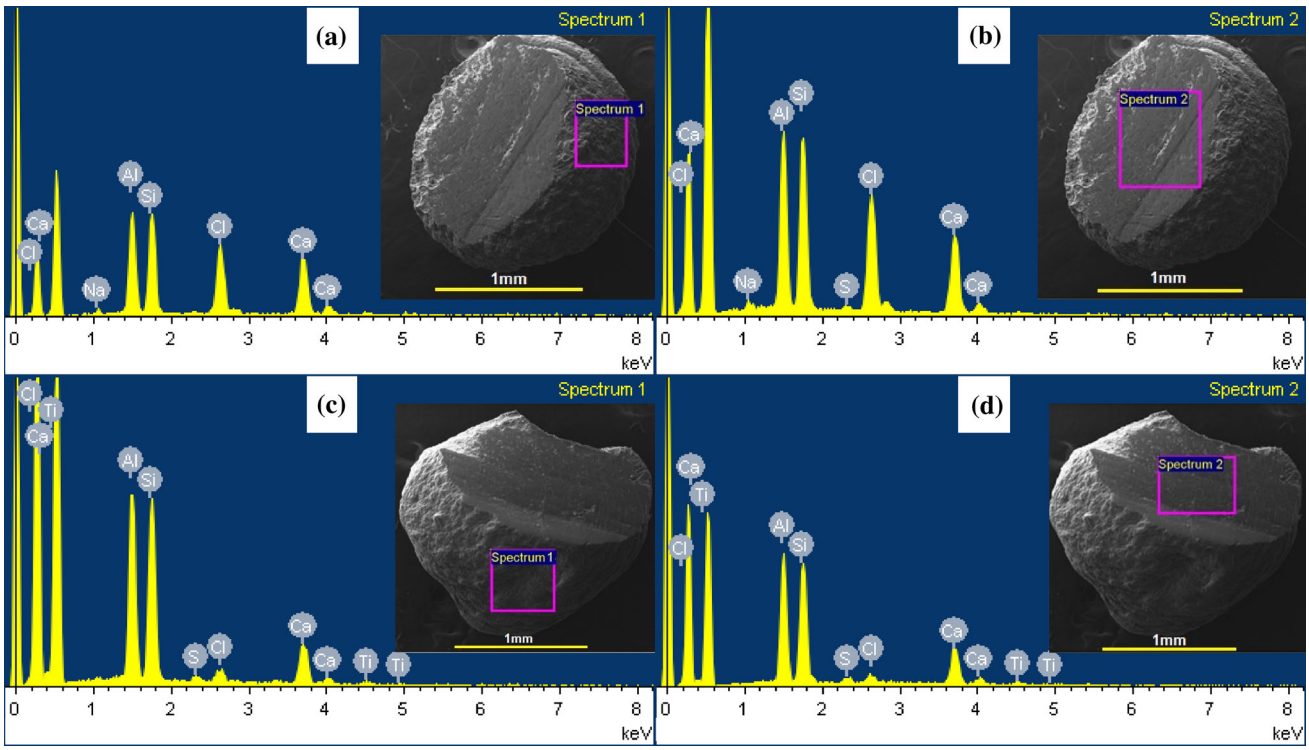

Fig. 5 SEM–EDS of beads (control containing 1 % CNC) without coating: **a** surface, **b** interior; with 2 % PEI coating: **c** surface, **d** interior

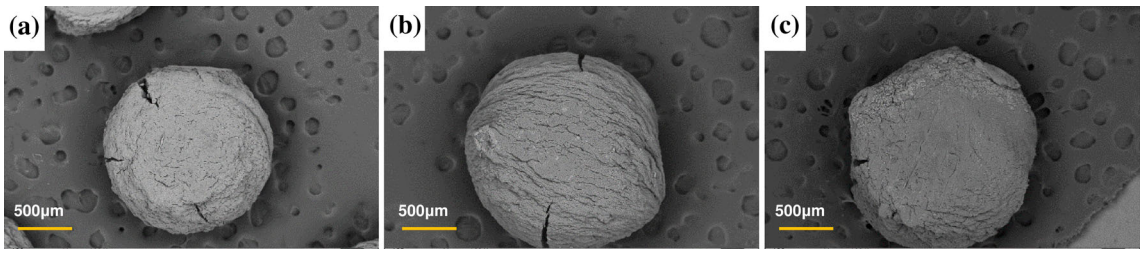

Fig. 6 Beads (control & 1 % CNC) surface morphology after compression by 10 kg force, **a** no coating, **b** 2 % PEI coating, **c** 4 % PEI coating

results. Most likely the positively charged imine groups of PEI successfully competed with and exchanged a portion of Ca^{2+} on the surface of beads by forming stronger electrostatic interactions with carboxylic groups. An additional factor was that PEI molecules were not able to penetrate the bead's interior, and thus, PEI coating could only affect the amount of Ca^{2+} found on the beads' surface. Simultaneously the weight percentage of Cl decreased upon coating. This could be attributed to Cl^{-} becoming dispersed in PEI solution during the coating process.

The surface morphology of a single bead changed somewhat after compression under an increasing force of 0–10 kg (Fig. 6). The beads were not completely crushed after withstanding 10 kg force (98.1 N), instead, they flattened, and cracks appeared at the edges. However, with more PEI coating on the surface, the beads tended to have less cracks.

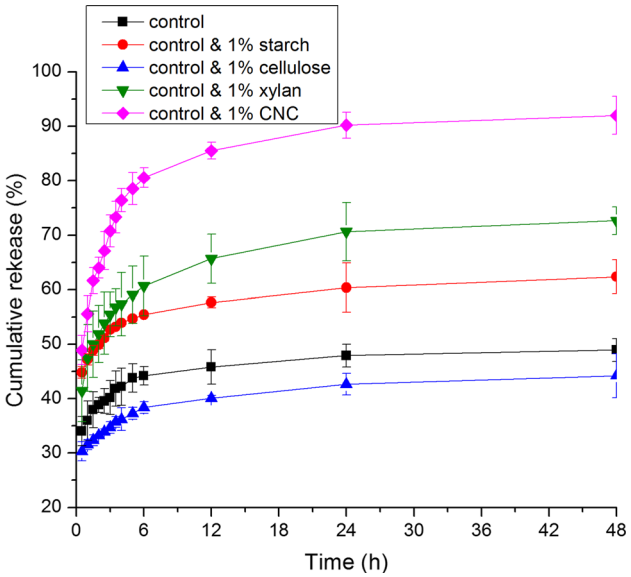

Fig. 7 Cumulative release of beads with no coating

Cumulative release analysis

The effects of the polysaccharide filler and the PEI solution concentration used for the coating were investigated in light of their controlled release capabilities. Figures 7 and 8 show the time release of PAA from beads of different compositions without or with further coating at different concentrations of PEI solutions. The time release of PAA was determined for a total of 48 h of release at fixed time intervals.

As can be seen from Fig. 7, there is an initial fast release (30–50 %) of PAA from the beads within the first 30 min regardless of the filler added to the control sample. This release may mainly be attributed to PAA molecules located at the open structure close to the bead surface when in contact with water. The cumulative release decreased after 6 h and remained stable after 24 h. At the end of 48 h, a portion of PAA was still trapped inside the beads probably due to the interaction with positive charges. The presence of CNC, xylan, or starch as fillers increased the PAA release rate compared with the control sample. This may indicate that these three polysaccharides either created a more open structure with alginate and kaolin or hindered the sites from forming electrostatic interactions with Ca^{2+} in the beads. It is also possible that the additional negatively charged carboxylic acid groups contributed by xylan may have formed stronger electrostatic interactions with Ca^{2+} and thus repelled some of the PAA during the crosslinking and release procedures. Similarly, the enhanced release of PAA by the xylan-containing beads could also result from repulsion of the PAA by the negatively charged carboxyl groups on the xylan. Thus, the release of PAA within the first 48 h could potentially be regulated by carefully designed polysaccharide combinations.

When the beads were coated with PEI, the surface layer acted as a barrier to the free passage of PAA during the initial 30 min to 48 h by forming a denser structure. Further, the outside layer may have extra positive charges originating from PEI which may hinder PAA from being readily released from the beads. From Fig. 8a, b, it can be seen that the cumulative release from beads composed of xylan and CNC decreased the most compared with all other samples. This could be interpreted as an indication that beads with xylan and CNC contained more PEI in their surface layer as discussed in the previous section.

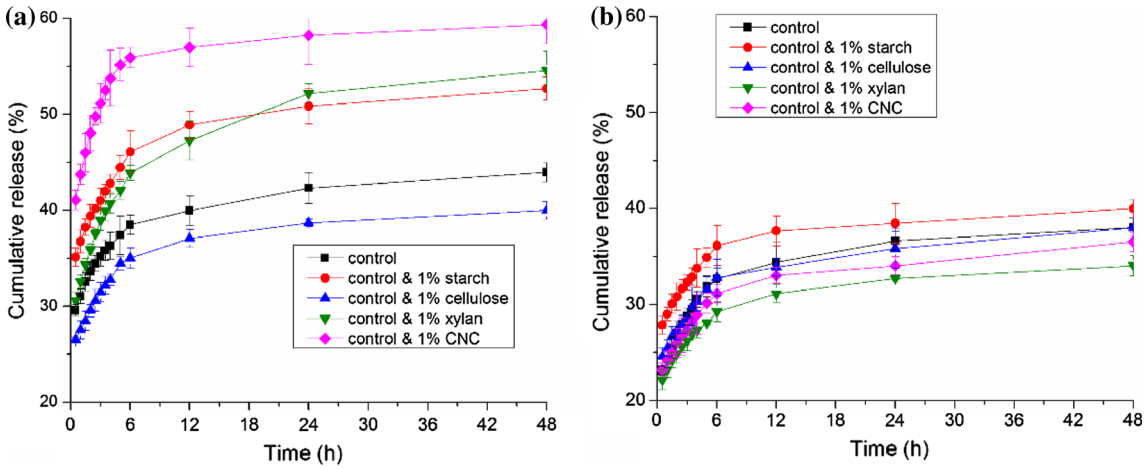

Fig. 8 Cumulative release of beads with **a** 2 % PEI coating, **b** 4 % PEI coating

Conclusion

In this research, a series of alginate- and kaolin-based beads were formed with added polysaccharide fillers, crosslinked in $CaCl_2$ solution and further coated in 2 or 4 % w/v PEI solution. Beads with PEI coating were slightly larger than beads without coating. PEI coating supported swelling of the surface layer due to its branched structure and affected the surface morphology of the beads. The cumulative release of a plant growth regulator, phenylacetic acid, clearly depended on the composition of the beads. The larger release rates of the beads that contained polysaccharide fillers indicated that the beads possessed a more open structure with hindered electrostatic interaction and larger repulsive force allowing more PAA to be released. The faster cumulative release by some polysaccharide combinations would be preferable when shorter release times are required. The PEI coating caused slowing of the release of PAA by forming a denser and positively charged surface layer. A steady release rate was reached before 48 h, and it is hypothesized that the release could be prolonged to longer time periods by careful selection of bead composition.

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