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Development of fertilizer coatings from polyglyoxylate-polyester blends responsive to root-driven pH change

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Abstract

Many current controlled released fertilizers (CRFs) are coated by non-biodegradable polymers that can contribute to microplastic pollution. Here, coatings of self-immolative poly(ethyl glyoxylate) (PEtG) capped with a carbamate and blended with polycaprolactone (PCL) or poly(L-lactic acid) (PLA) were evaluated. They were designed to depolymerize and release fertilizer in the vicinity of plant roots, where the pH is lower than in the surrounding environment. PEtG:PCL coatings exhibited significant temperature and pH effects, requiring 18 days at pH 5 and 30 °C, compared to 77 days at pH 7 and 22 °C to reach 15% mass loss. Plant roots were also effective in triggering the coating degradation. Spray coating and melt coating were explored with the latter being more effective in providing pellets that retained the urea prior to polymer degradation. Finally, PEtG:PCL coated pellets promoted plant growth to a similar degree or better than currently available CRFs.

Keywords: controlled release fertilizer, self-immolative polymer, biodegradation, poly(ethyl glyoxylate), microplastic, pH-responsive

Introduction

Fertilizer is typically applied to soil prior to peak plant nutrient demand, and in the interim it can be lost readily via leaching or volatilization.¹⁻³ Therefore, for traditional water-soluble fertilizers, the nutrient use efficiency (NUE), defined as the percentage of a nutrient that contributes to biomass production, is often low. For example, the NUE for nitrogen ranges from 30-50%.^{4,5} To compensate for low NUE and to maximize crop yield, excessive amounts of fertilizer are frequently applied.^{6,7} Excess fertilizer can contaminate surrounding ecosystems, causing

eutrophication, loss of biodiversity, and increased greenhouse gas emissions.^{8,9} Controlled release fertilizers (CRFs) can increase NUE and minimize the release of fertilizer into the surrounding environment.¹⁰ In CRFs, a coating often provides a protective barrier against water, thereby delaying nutrient release.

Typical CRF coatings are made of polymers such as polyethylene and polyurethane.^{11, 12} As these polymers are not biodegradable, they can result in the accumulation of microplastics in the environment.^{13, 14} To address this, there has growing interest in the development of biodegradable fertilizer coatings.¹⁵ For example, Lubkowski *et al.* developed coatings based on biodegradable poly(butylene succinate) and related polymers,¹⁶ and Costa *et al.* reported coatings based on polyhydroxybutyrate and ethyl cellulose.¹⁷ In addition, despite improvements in NUE for current CRFs compared to conventional fertilizers, their release is not directly triggered by plant nutrient demand. The timing of nutrient release generally depends on environmental conditions (primarily temperature), soil type, and coating thickness.^{18, 19} Therefore, CRFs may release nutrients in soil patches that have not yet been explored by plant roots. To enhance their efficiency, fertilizer coatings that release nutrients under specific conditions have been explored. For example, Feng *et al.* reported “smart” fertilizer coatings based poly(*N,N*-dimethylaminoethyl methacrylate) that released nutrients in a pH and temperature-responsive manner.²⁰ Other nanotechnology-based solutions have also been proposed and explored.²¹ To optimize nutrient delivery, a stimulus-responsive coating ideally would release fertilizer directly in response to the presence of active plant roots, and further research is still needed to achieve this.

Self-immolative polymers (SIPs) are a new class of stimuli-responsive polymers that degrade through end-to-end depolymerization after either backbone cleavage or end-cap removal in response to a specific stimulus.²²⁻²⁴ Because of their controlled and triggerable degradation, SIP

use in fertilizer coatings could potentially increase the synchronization of fertilizer release with plant growth. The SIP poly(ethyl glyoxylate) (PEtG) is of particular interest for agricultural applications, because it degrades into glyoxylic acid hydrate and ethanol (Figure 1A), compounds that can be readily metabolized in the environment and therefore should exhibit low ecotoxicity.²⁵⁻²⁷ In addition, PEtG end-caps can be designed to respond to a variety of stimuli, including change in temperature or pH, light, or various chemical species.^{25, 28-30} Thus, there is the potential to develop PEtG as a fertilizer pellet coating to improve nutrient delivery, while avoiding the use of non-biodegradable polymers that accumulate as microplastics in the environment.

Figure 1. A) Schematic illustrating the degradation of PEtG under acidic conditions; B) Schematic illustrating the function of a triggerable fertilizer coating.

Chemical reactions in many organisms are accompanied by decreases in pH, which makes change in pH a possible target stimulus for triggering the degradation of coatings.^{31, 32} Plant roots release exudates into their immediate environment (the rhizosphere), and these exudates contain high levels of organic acids, sugars, amino acids, inorganic molecules and enzymes.³³ In addition, as plants take in cationic nutrients, they release H^+ ions into the soil to balance charges, which causes acidification of the soil around the plant root.^{34, 35} To take advantage of root zone

acidification as a signal for the presence of plant roots, we incorporated a phenyl carbamate end-cap for PEG that has a preference for cleavage at acidic over neutral pH (Figure 1B).³⁶ The polyacetal backbone of PEG also should be cleaved more rapidly at acidic pH, leading to subsequent depolymerization.³⁷ However, because PEG has a glass transition temperature of less than 0 °C,²⁵ it is rubbery and tacky at room temperature, and the use of pure PEG as a fertilizer coating would result in the undesirable aggregation of pellets. Based on prior work in our groups,³⁸ which explored the effects of blending on the properties of PEG, in the currently described work we used 50 wt% of either poly(L-lactic acid) (PLA) or polycaprolactone (PCL) blended with PEG to provide mechanically robust and non-adhesive coatings. The responses of the coatings to chemical and plant root stimuli, as well as the release properties of the coated urea pellets, were evaluated. Creeping bentgrass (*Agrostis stolonifera*) was selected as a test species, because grasses have high densities of roots and therefore may provide an effective stimulus for fertilizer release.³⁹ The triggering of coating degradation by creeping bentgrass roots was studied. Finally, plant growth studies were conducted to examine the effectiveness of different coating methods for a range of fertilization treatments and soil types. To the best of our knowledge, this paper presents the first study of an SIP used for fertilizer coating applications.

Experimental section

General materials

All chemicals were purchased from commercial suppliers and used without further purification unless otherwise noted. PEG end-capped with a phenyl carbamate was synthesized as previously reported.²⁵ The specific batch used for this work had a number average molar mass (M_n) of 34 kg/mol and a dispersity ($\bar{D}$) of 1.4. The PLA used was a standard filament with no added

plasticizers or colorants, an M_n of 103 kg/mol, a D of 2.56, and was purchased from 3D Solutech. PCL was supplied by Scientific Polymer Products and had an M_n of 55 kg/mol. Dichloromethane was purchased from Caledon Laboratory Chemicals. Urea was purchased from the Tractor Supply Company (London, Ontario, Canada) and consisted of commercial grade urea with a mean diameter of 4.3 mm and mass of ~60 mg per pellet. Modified half-strength Hoagland's solution that lacked sources of nitrogen was prepared⁴⁰ (i.e. all nitrogen was supplied directly from the urea treatment). Macronutrients had concentrations of 200 mM K_2SO_4 , 200 mM $CaCl_2 \cdot 2H_2O$, 100 mM KH_2PO_4 , 50 mM $MgSO_4 \cdot 8H_2O$ and 1 mM Fe-EDTA. Micronutrients had concentrations of 0.25 mM NaH_2PO_4 , 0.05 mM $CoCl_2 \cdot 6H_2O$, 1.25 mM H_3BO_3 , 1 mM $MnSO_4 \cdot H_2O$, 1 mM $ZnSO_4 \cdot 7H_2O$, 0.025mM $CuSO_4 \cdot H_2O$, and 0.025 mM $Na_2MoO_4 \cdot 2 H_2O$.

Preparation of PEtG blend films

PEtG, PLA and PCL were separately dissolved in CH_2Cl_2 at 90 mg/mL. Both PEtG:PLA and PEtG:PCL were combined separately in 50:50 ratios by stirring inside glass vials at 800 rpm for 20 min. The blends were then drop-cast into glass vials or onto slides and the solvent was evaporated *in vacuo* for 24 h. The film thickness, measured using digital calipers, was ~ 150 μm and the surface area was ~2 cm^2 . Each film had a total mass of ~30 mg (weighed accurately).

Degradation of PEtG blend films in aqueous buffer solutions

The initial masses of the films were measured and recorded. For each treatment combination, triplicate samples were prepared for each of the ~10 time points. The polymer films were immersed in 15 mL of 0.1 M aqueous buffer solution (citrate buffer for pH 5 and phosphate buffer for pH 7) at 30 °C or 22 °C. Treatments at 30 °C were placed inside a temperature-controlled incubator, while the 22 °C samples were placed inside a storage cabinet. All samples were stored in the dark and were capped to avoid evaporation. Periodically, 3 films for each pH and temperature treatment

were removed from the buffer solution, rinsed with distilled water, dried in a lyophilizer for 24 h, then reweighed. The percent initial mass for each film was calculated as:

$$\% \text{ initial mass} = (\text{mass at sampling time} / \text{initial mass}) \times 100\%$$

For comparing degradation among samples, the number of days needed to reach a mass loss threshold of 15% was used as the response variable.

Degradation of PEtG blend films in clay-loam agricultural soil

Soil was collected from an agricultural field in southern Ontario, Canada, at the Environmental Sciences Western field station (43°4'30"N, 81°20'11"W). The soil texture was classified as a well to imperfectly drained silt loam and loam glacial till, with an average pH of 7.44, soil organic matter content of 8.24%, and total C and N contents of 2.84% and 0.22%, respectively.⁴¹ The soil was dried at 60 °C for 72 h. Two kilograms of soil were added to each of 2.5 L tubs and adjusted to either pH 5 or 7 using citrate buffer and phosphate buffer and to 20% moisture content. The resulting soil pH was assessed using an electrode pH meter immersed into a slurry formed from a 10 g subsample of soil in 100 mL of water. Samples were prepared similarly to the solution degradation study above; however, they were drop cast onto glass slides instead of vials. The slides were placed in nylon bags and immersed in the tubs with soil (30 slides per tub). The boxes were sealed to minimize evaporation and were rehydrated occasionally to compensate for any moisture loss. Periodically, three replicate slides were collected for each treatment and were rinsed with H₂O to remove the soil. The films were transferred to vials, dried on a lyophilizer for 24 h, and then weighed. Polymer mass loss was assessed as described. For comparing degradation among samples, the number of days needed to reach a mass loss threshold of 15% was assessed.

Degradation of PEtG blend films exposed to plant roots

All treatments were carried out in growth chambers under the following conditions. 420 g of quartz-based gravel substrate (approximately 2 mm diameter) was placed into each of 120 pots (10 cm by 10 cm in size). Creeping bentgrass was seeded at 2.44 g/m² into 80 pots and was left to germinate for 10 d prior to experimentation. A citrate buffer solution (pH 5, 0.1 M) was added weekly at 50 mL per pot for the pH-stimulated treatments for 40 pots. The remaining 40 pots were used as controls, and they contained polymeric films and gravel substrate. Two growth chambers provided 16 h of light and 8 h of darkness at a relative humidity of 70% at either 30 °C or 22 °C. The pots were fertilized once a week for a total of 50 d with 50 mL of half-strength modified Hoagland's solution that contained both macronutrients and micronutrients, but was lacking nitrogen. Urea was applied at 58 kg/ha in the form of urea for all treatments and all pots were watered every other day. Films were prepared as described above, drop cast onto half-microscope slides. Polymeric films were inserted 3 cm under the gravel substrate for all treatments. Four replicate films per treatment were removed periodically for a total of 5 time points over 40 d and were rinsed with H₂O to remove the gravel. The films were transferred to vials, dried on a lyophilizer for 24 h, and then weighed. Mass loss determination and analyses were as described above.

Fourier transform infrared spectra - attenuated total reflectance (FTIR-ATR)

FTIR-ATR spectra were obtained on a PerkinElmer Spectrum Two FTIR Spectrometer using the attenuated total reflectance accessory. Coated pellets were frozen with liquid N₂ to enable crushing into a fine powder with a mortar and pestle. The powder was then inserted into the instrument.

Surface morphology

Scanning electron microscopy (SEM) was performed to study the morphology of the coated polymer surfaces using a Hitachi S-3400N instrument at a voltage of 3 kV (Hitachi, Tokyo, Japan).

The samples were mounted on carbon taped aluminum stubs and sputtered with gold at a rate of 5 nm/min for 4 min (Hummer-6 sputtering system, Anatech, Union City, California). The overall surface morphology was examined at a resolution of 30 μm under 3 kV.

Preparation of spray coated urea

Polymer blends of PEtG:PCL (50:50 mass ratio) were dissolved in CH_2Cl_2 at 10 mg/mL. 40 g of urea pellets were added to a 15 cm diameter pan coater (Arthur Colton Co. 210664, Detroit, Michigan). Metal baffles were added to the inside of the pan coater to increase the rotation of the urea bed. Polymeric mixtures were added to a 250 mL Erlenmeyer flask with a 24/40 connection. A standard thin layer chromatography (TLC) reagent sprayer was inserted into the flask and was attached to the house air within a fume hood. The polymeric blend mixture was sprayed from the TLC sprayer at a rate of 5 mL/min onto the rotating bed of urea at 30 rpm, which was sufficient to maintain a slumping bed. Urea was sprayed until there was 5 wt% of polymeric material on each urea particle. Coating thickness was approximately 80 μm , measured using a digital caliper, and coating integrity was tested by placing pellets in water for 72 h.

Preparation of melt-coated urea

PEtG:PCL (50:50 mass ratio) was first dissolved in CH_2Cl_2 at 90 mg/mL in a beaker. Solvent was evaporated *in vacuo* for 48 h. The polymeric material was then immersed in a water bath set at 60 $^\circ\text{C}$ for 20 min. Once the material was melted, it was scooped using a glass rod, applied to urea pellets (60 mg), and hand rolled to produce spherical coated pellets. Polymeric coatings were on average 800 – 1000 μm in thickness, as measured using a digital caliper, and coating integrity was tested by placing pellets in water for 72 h.

Determination of urea release rates in solution

Melt-coated PEG:PCL urea pellets were placed into vials ($n = 3$) with either 10 mL citrate (pH 5) or phosphate buffer (pH 7). The vials were sealed with paraffin wax and stored at 22 °C or 30 °C. Periodically, over a 21 d period, the urea samples were removed and placed into new vials with fresh buffer solution. The initial solution was then measured for nitrogen content to determine the release rate of urea resulting from polymeric coating degradation. Total nitrogen was measured by persulfate oxidation, followed by analysis for NO_3^- using a SmartChem 140 discrete auto analyzer (Westco Scientific Instruments Brookfield, CT). Oxidizing reagent was prepared following the procedure of Cabrera and Beare.⁴² A combination of 1.85 M $\text{K}_2\text{S}_2\text{O}_8$ and 3.86 M of H_3BO_4 were dissolved in 50 mL of 3.75 M of NaOH, and the flask was then topped up to 500 mL with distilled-deionized water. Urea samples were diluted by 710-fold and pipetted into glass tubes with Teflon screw caps. Oxidizing reagent was added and the tubes were secured tightly. The tubes were then placed in an autoclave at 120 °C for 20 min and subsequently analyzed for NO_3^- .

Plant growth responses to coated and uncoated urea in soil and potting mix

Plant growth responses to PEG coated pellets were examined in soil or potting mix under a range of growing conditions and fertilization treatments. Urea pellets were prepared using the methods noted above for melt-coated PEG:PCL blends. Slow release urea (ESN) was supplied by Agrium (Agromart, Thorndale, ON). Both uncoated urea and no urea were used as controls. For each pot, 240 mg of urea was used (58 kg/ha). Pots ($n = 10$ per treatment) were supplemented with ~ 420 g of either 1:1 of the clay-loam soil (see properties above) to perlite or 1:1 Pro-Mix BX growing medium (Premier Horticulture Inc., Quakertown, PA, USA) to fine grade sand. Urea was added to the pots and mixed into the soil manually at the same time as seeding. Creeping bentgrass (*Agrostis stolonifera*) was seeded at 2.44 g/m². Pots were fertilized once a week for total of 5 weeks with 50

mL of modified Hoagland's solution that contained both essential macronutrients and micronutrients, but that lacked any source of nitrogen.

Plant growth in response to melt-coated PEG:PCL pellets was compared to that in response to either a no fertilization control, an uncoated fast-release urea control or to a commercially available slow-release fertilizer (ESN) ($n = 10$). Under greenhouse conditions, creeping bentgrass was grown in a 1:1 clay-loam soil to perlite mixture. In a second experiment designed to test interactions with substrate, creeping bentgrass was grown outdoors under ambient weather conditions in a common garden experiment in pots filled with either a 1:1 clay-loam soil to perlite mixture or a 1:1 Pro-Mix BX growing medium to sand mixture. For all experiments, plant dry shoot and root biomass were recorded after a 5-week growing period. Greenhouse temperatures were variable and ranged between 22 – 30 °C during the month of June, while outdoor temperatures followed historic averages in London, ON, with the average temperature ranging between 13.2 ± 0.6 °C and 24.3 ± 0.7 °C during this time.⁴³ Plants grown under greenhouse conditions were watered daily for 5 weeks, while outdoor plants were watered on days that it did not rain during the month of June. After 5 weeks, shoot biomass was clipped and placed into envelopes. The shoots were then dried at 60 °C for 72 h and dry mass was recorded for each treatment. Roots were removed from the pots, rinsed with water, dried at 60 °C in envelopes for 72 h, then weighed.

Data analyses

Two-way analysis of variance (ANOVA) was used to assess the effects of temperature and pH on mass loss and urea release. The number of days needed to reach a mass loss threshold of 15 wt% was used as a response variable for comparing mass loss among samples (this threshold was exceeded for all degradation trials). One-way ANOVA was used to analyze plant shoot and root

biomass responses for the growth experiments, with the significance of pairwise treatment differences assessed using Tukey's HSD tests. All statistical analyses were conducted using JMP version 14 (SAS Institute).

Results and Discussion

Mass loss profiles of films immersed in buffer solutions

The degradation of coatings composed of pure phenyl carbamate end-capped PEG, as well as the 50:50 blends (PEG:PCL and PEG:PLA), were characterized first in buffer solutions. Films were stored at different temperatures (either 22 °C or 30 °C) and pH conditions (citrate buffer at pH 5 and phosphate buffer at pH 7). These conditions were selected to reflect the range of conditions experienced by the plant roots in the field during the early-mid growing season. Temperature dominates many physicochemical processes, such as polymer degradation. Therefore, we expected bond cleavage and backbone depolymerization to increase with increasing temperature. Soil pH is commonly close to 7, because soil is composed of alkaline and silica based materials. To confirm the extent of root zone acidification resulting from the cationic exchange of nutrients, a pH indicator agar-film was used to visualize the acidification of the rhizosphere following the procedure described by Zhou *et al.*⁴⁴ After immersion of the roots in the gel for 72 h, the gel turned yellow, indicating a pH of ~5 (Figure S1). Therefore, a pH of 5 was also investigated.

For pure PEG, both high temperature ($P < 0.001$) and low pH ($P < 0.001$) decreased the time required to reach 15% mass loss (22 °C/pH 7 – 63 d, 22 °C/pH 5 – 47 d, 30 °C/pH 7 – 32 d, 30 °C/pH 5 – 17 d; Figure 2A). A threshold of 15% mass loss was used, because rapid degradation generally occurred after this phase. Similarly, for PEG:PCL both high temperature ($P < 0.001$) and low pH ($P < 0.001$) decreased the number of days required to reach 15% mass loss (22 °C/pH

246 7 – 77 d, 22 °C/pH 5 – 54 d, 30 °C/pH 7 – 33 d, 30 °C/pH 5 – 18 d; Figure 2B). For both pure
247 PEtG and PEtG:PCL, temperature and pH also displayed a significant interaction ($P = 0.0002$),
248 indicating that the magnitude of the pH effect was conditional on the temperature treatment level.
249 PEtG:PLA underwent more constant degradation than pure PEtG and PEtG:PCL. Moreover, while
250 there was a significant temperature effect on the number of days required to reach 15% mass loss
251 for the PEtG:PLA blend ($P < 0.002$; 22 °C – 53 d/pH 5, 30 °C/pH 5 – 18 d; Figure 2C), there was
252 no significant effect of pH on degradation ($P = 1.0$).

Figure 2. Mass loss profiles for coatings immersed in buffers at pH 5 or 7 and either 22 °C or 30 °C: A) Pure phenyl carbamate end-capped PEtG; B) PEtG:PCL; C) PEtG:PLA. Dotted lines

represent the threshold of 15% mass loss used for analysis (n= 3 for each time-point, with error bars denoting standard deviation).

Most PEG:PCL treatments exhibited a final mass loss of ~50 % at 30 °C and at low pH, which indicated that the PCL component was not degrading over the time frame of the experiment. This was expected, because the degradation of PCL is typically very slow *in vitro*.⁴⁵ Though pH dependence was not statistically significant for all treatments, a trend of reduced degradation was observed in the samples exposed to pH 7 at room temperature. PLA did not reach 50% mass loss in most treatments. It is possible that the microscale phase separation of PLA and PEG may shield some domains of PEG from degradation.³⁸

Overall, PEG degradation was temperature-dependent for all treatments, with higher mass loss observed at 30 °C than at 22 °C. The temperature effect can be attributed to the increased rate of end-cap and backbone cleavage, as well as depolymerization at higher temperature. However, it was only pH dependent, with increased mass loss at pH 5, for the pure PEG and the PCL blends. The pure PEG and PEG:PCL blends exhibited delayed degradation until they reached a critical threshold and then underwent rapid degradation similar to that observed in a bulk degradation process. In contrast, the PEG:PLA blends exhibited more constant, gradual degradation consistent with surface erosion theory.⁴⁶ While we did not explicitly study the morphology changes occurring in the coatings in the current work, our previous studies involving scanning electron microscopy on ultraviolet light-responsive PEG:PLA and PEG:PCL blend films indicated the appearance of micrometer-sized pores as the PEG domains eroded, leaving the polyester domains to undergo a slower degradation process.³⁸

Mass loss profiles of films exposed to buffered agricultural soil

278 Because the target application of these polymers is for coating fertilizer pellets, we investigated
279 the degradation of the PEtG blends in locally-sourced agricultural soil. Pure PEtG was not
280 investigated, because as noted above, its properties are unsuitable for coating development. The
281 initial soil pH was ~ 7.5 , and it was adjusted to pH 7 and pH 5 using buffer solutions. The soil was
282 maintained at 20 wt% moisture content. For PEtG:PCL, high temperature ($P < 0.001$) decreased
283 the number of days required to reach 15% mass loss and pH had no significant effect on
284 degradation at high temperature, whereas there was a slight pH effect at the lower temperature (P
285 $= 0.027$; 22 °C/pH 7 – 60 d, 22 °C/pH 5 – 54 d, 30 °C/pH 7 – 17 d, 30 °C/pH 5 – 15 d; Figure 3A).
286 Likewise, for the PEtG:PLA blend, there was a significant temperature effect on the number of
287 days required to reach 15% mass loss ($P < 0.001$; 22 °C/pH 7 – 29 d, 22 °C/pH 5 – 35 d, 30 °C/pH
288 7 – 18 d, 30 °C/pH 5 – 18 d; Figure 3B), but no significant effect of pH on degradation ($P = 0.5$).

Figure 3. Mass loss profiles for coatings immersed in agricultural clay-loam soil with pH adjusted to either pH 5 (0.1 M citrate acid) or pH 7 (0.1 M phosphate) at 22 °C or 30 °C: A) PETg:PCL; B) PETg:PLA. Dotted lines represent the threshold of 15% mass loss used for analysis (n= 3 for each time-point, with error bars denoting standard deviation).

Overall, significant temperature dependence was observed across all treatments, which was similar to the buffer solution treatments. However, there was no apparent dependence on pH for the PCL treatments at elevated temperature. The reason for this result is not entirely clear, but it may have arisen from the delicate balance between rate-limiting end-cap cleavage and rate-limiting depolymerization. While cleavage of the carbamate end-cap should increase with

increasing acidity, depolymerization exhibits a rate minimum at pH 5.⁴⁷ It is also possible that the pH response was muted as a result of the strong buffering capacity of the soil. Furthermore, it was noted that both blends exhibited more steady mass loss than was observed in the buffer immersion study, where there was an initial plateau followed by rapid mass loss. This disparity likely can be explained by the differences in water content between the soil and buffer solution. We previously have shown that when mass loss studies were performed in water, there was a plateau in mass loss arising from the trapping of ethyl glyoxylate hydrate within the eroding polymer film.⁴⁷ When mass loss studies were performed in air, this plateau was not observed. Thus, due to their lower water content, the degradation trials in soil more closely resembled the degradation in the dry state.

Mass loss profiles of coatings exposed to plant roots

The degradation of the PEG:PCL and PEG:PLA coatings in response to the presence of creeping bentgrass roots was examined in a silica-based gravel substrate. Roots became embedded in the polymer film after 40 d. These trials also were carried out at temperatures of 22 or 30 °C. Based on the results of the root zone acidification experiment, roots were expected to acidify the soil in their vicinity and increase the rate of coating degradation compared to the (no root) control. A positive control was established using pH 5 citrate acid buffer applied weekly to the films in the gravel substrate. The films were incubated in growth chambers kept at 70% humidity, and for the 30 °C treatment, the temperature was reduced to 22 °C at night to simulate natural daily temperature fluctuations.

For the PEG:PCL coatings, there was a significant interaction between temperature and plant roots ($P = 0.019$), with high temperature combined with the presence of plant roots or the pH 5 buffer control decreasing the number of days required to reach 15% mass loss compared to no stimulus (22 °C/gravel control – 32 d, 22 °C/pH 5 – 32 d, 22 °C/plant roots – 32 d, 30 °C/gravel

control – 26 d, 30 °C/pH 5 – 7 d, 30 °C/plant roots – 7 d; Figure 4A). For the PETG:PLA blend, while there was a significant temperature effect on the number of days required to reach 15% mass loss ($P < 0.0001$; 22 °C/plant roots – 40 d, 30 °C/plant roots – 26 d; Figure 4B), there was no significant difference between the plant root treatment, the pH 5 buffer control, and the no stimulus control. Thus, these PLA blended films behaved similarly to those in the buffer solution and soil trials, indicating that the PLA may have slowed degradation, resulting in pH independence.

Figure 4. Mass loss profiles for coatings imbedded in pots with either creeping bentgrass roots, gravel substrate alone, or weekly dosages of 0.1 M pH 5 citrate buffer at 22 °C or 30 °C: A)

PEtG:PCL; B) PEtG:PLA; Pots were stored in growth chambers with 16 h of light, and 8 hours of darkness under 70% humidity. Dotted lines represent the threshold for degradation at 15 wt% mass loss (n = 4 for each time-point, with error bars denoting standard deviation).

Based on the above results, PEtG:PCL blend films appear to be best-suited for the development of fertilizer coatings, given that they responded to both low pH and elevated temperatures, whereas the PLA blends were only temperature dependent. In addition, PCL tended to be stable before undergoing rapid degradation, whereas PLA samples underwent constant gradual degradation. Polymeric coatings for fertilizer pellets would likely improve plant nutrient delivery by exhibiting a stable phase after soil application, followed by triggering and degradation.

The longevity of the polymer blends in the absence of stimulus (i.e. shelf life) also was important to assess, so we prepared polymer blends in vials. These films were exposed to air at room temperature (21 °C) and were weighed periodically to assess mass loss. The blends were stable, with no mass loss recorded for PEtG:PLA for at least 270 d (at least 320 d for PEtG:PCL) (Figure S2). These initial results suggest that the polymeric blend will be stable at room temperature and will not undergo premature depolymerization during storage, prior to soil application.

Preparation and analysis of coated fertilizer pellets

Spray coated films were applied to urea pellets by dissolving PEtG with PLA or PCL in CH₂Cl₂ at 10 mg/mL and spraying the resulting solution via a chemical reagent sprayer in a rotating pan coater. PEtG:PCL blends also were melted together at 60 °C and manually coated onto urea pellets. The pellets were immersed in water to visualize urea leakage, which was indicated by the formation of hollow capsules that floated to the surface. In addition, SEM was used to examine

the integrity of the coatings. Images of commercially available controlled release fertilizer also were examined for comparison (Figure S3).

In initial work, we observed that water penetrated the spray-coated pellets quickly once they were immersed in water, resulting in rapid urea release. To reduce water penetration, we examined the incorporation of 5 wt% paraffin wax into the PEtG:PCL blend. This approach has been used previously to compensate for defects that occurred during the preparation of polyurethane coated pellets.⁴⁸ However, the addition of paraffin worsened the integrity of our coatings, producing more holes (Figure S4A), and the pellets also started to stick together within the pan coater, causing tearing. This likely occurred due to the CH₂Cl₂ becoming trapped within the paraffin wax matrix, reducing the rate of solvent evaporation (Figure S4B). Once the wax was removed from the formulation we were able to produce coatings that were thicker and had fewer defects. The PEtG:PCL coated pellets lasted in water for a week before water penetration began. The coatings were smooth, but there were still small defects distributed throughout (Figure 5A).

Figure 5. SEM images of PETG:PCL coated urea pellets prepared by: A) Spray coating and B) Melt-coated PETG:PCL blend.

Solvent annealing as well as temperature annealing were then investigated in an attempt to reduce the holes that appeared during preparation. Through exposure to vapors of CH_2Cl_2 or CHCl_3 , it was anticipated that the polymer would soften and become sufficiently mobile to fill in the imperfections. However, based on SEM no notable improvements occurred and in some cases more defects appeared (Figure S5). We thus concluded that we were unable to improve the polymer properties through solvent annealing practices for the PCL blends, and indeed, these techniques caused more damage to the overall film surface structure. Thermal annealing of the coatings above the melting temperature (T_m) of PCL (60 °C) did not result in any improvements. Similar results were obtained for the PETG:PLA spray-coated pellets (Figure S6). Overall, based on the residual material recovered from the coating pan, the spray coating process had an efficiency of 50 - 60%.

While the spray coating process still might be optimized using a fluidized bed or related technology, for the current study, suitable coated pellets could be prepared from melted PEG:PCL blends ($> 60\text{ }^{\circ}\text{C}$) through a manual process. The surface morphology achieved using this technique appeared rough, but the coatings did not have any noticeable holes, which was crucial for preventing premature urea leakage (Figure 5B). The pellets were stable in water (at room temperature) for almost 30 d before water penetration occurred, which was a substantial improvement relative to the spray-coated pellets. This stability can likely be attributed to their thickness of $\sim 800 - 1000\text{ }\mu\text{m}$, compared to $\sim 80\text{ }\mu\text{m}$ for the spray-coated films, as measured by calipers. Coating efficiency was estimated to be near 100% for this method, because essentially all of the material was incorporated onto the pellets.

The spray (PEG:PLA) and melt (PEG:PCL) coated pellets were characterized using FT-IR spectroscopy (Figure 6). Urea bands were confirmed by the presence of N-H stretches at $\sim 3340\text{ cm}^{-1}$ and between $1457\text{--}1696\text{ cm}^{-1}$ in both coatings. PEG, PLA, and PCL all contained very similar vibrational bands, with their presence confirmed by peaks corresponding to C-H and C=O stretches at $2962\text{--}2934\text{ cm}^{-1}$ and $1717\text{--}1741\text{ cm}^{-1}$ respectively.

Figure 6. IR spectra of melt-coated PETG:PCL and spray coated PETG:PLA urea pellets showing peaks from urea ($\sim 3340\text{ cm}^{-1}$ and between $1457\text{-}1696\text{ cm}^{-1}$), as well as PETG and the corresponding polyester ($2962\text{-}2934\text{ cm}^{-1}$ and $1717\text{-}1741\text{ cm}^{-1}$).

Urea release from pellets

Because of their stability in aqueous solution, the release of urea from the melt-coated PETG:PCL pellets was studied. Sprayed coated pellets, as noted above, exhibited leakiness due to water penetration through holes in the coating, and were deemed unsuitable for further studies. The pellets were placed into vials in either pH 5 or pH 7 buffer solution and were stored at $22\text{ }^{\circ}\text{C}$ or $30\text{ }^{\circ}\text{C}$. The release of urea into the buffer solution was measured. A small number of pellets that leaked within the first 5 d were deemed defective due to premature structural failure and thus were omitted from the results. The release rate of urea followed similar trends to the coating mass loss profiles with respect to temperature dependence; as the temperature increased, more urea was released, indicating coating degradation (Figure 7). However, in general the urea release occurred more rapidly than the mass loss, as a single breach in the coating would be sufficient to result in

complete urea release from a pellet. After 21 d, there was a significant temperature effect ($P < 0.001$), with almost 100% urea release for the 30 °C treatments, whereas only ~20% was released at 22 °C. However, the release rate was not pH-dependent ($P = 0.8$) (Figure 7). The lack of significant pH dependence may have arisen in part from the large sample variability. This variability at 30 °C may have resulted from the higher temperature hastening the failure of semi-defective pellets (i.e., thinly coated regions rapidly degraded). Indeed, cross-sectional images of coated pellets showed some variation in coating thickness across the pellet (Figure S7). Temperature and pH showed no significant interaction ($P = 0.7$).

Figure 7. Urea release from PEtG:PCL coated pellets exposed to citrate buffer (pH 5) or phosphate buffer (pH 7) at either 22 °C or 30 °C for 21 d ($n = 3$ for each time-point, with error bars denoting standard deviation).

Although no significant pH dependence was observed, the coatings nevertheless delayed urea release over the 20 d period. However, we could not quantify how much degradation of the polymeric material had to occur to enable water penetration. There may have been as little as 5% mass loss from the coating before water penetration occurred and released the urea. It should also

be noted that agricultural field applications for the coated urea pellets would not generally involve their complete immersion water (required here to maintain constant temperature and pH) and thus the observed release rates of urea measured in this experiment can be considered as upper limits. However, the results indicate that we have developed a coating that is stable at 22 °C, responsive to temperature increase and releases urea slowly over time displaying characteristics similar to slow-release fertilizers, which ultimately could increase nutrient release synchronization with plant needs.

Plant growth experiments

Plant growth was compared for creeping bentgrass treated with melt-coated PEG:PCL pellets, no urea, uncoated urea pellets, and commercial controlled release fertilizer pellets (ESN). ESN has been characterized to release 80% of its N content over 30 d to 60 d at 23°C, and exhibits more rapid release at higher temperatures (e.g. greater than 80% N released within 25 d at 30 °C).⁴⁹ The effects under different conditions including greenhouse versus outdoors, and different soil types were explored. A preliminary experiment investigating the effects of different nitrogen application rates on the growth of creeping bentgrass was performed and based on this study an application rate of 58 kg/ha of urea was selected (Figure S8).

There were significant treatment effects on the aboveground biomass of greenhouse-grown creeping bentgrass (Figure 8A). Both the uncoated pellets, and commercial ESN pellets resulted in more than a doubling of aboveground biomass relative to the no fertilization control, and the melt-coated PEG:PCL blends resulted in almost triple the aboveground biomass. Belowground biomass analysis demonstrated the fertilization treatments had no differential effects on root growth (Figure S9). Therefore, the results hereafter focus on the aboveground biomass responses.

Figure 8. Aboveground biomass of creeping bentgrass, comparing melt-coated PEtG:PCL pellets, to either no pellet (control), uncoated fast release urea, or ESN. A) Pots were stored in a greenhouse. The substrate consisted of 1:1 clay-loam soil:perlite. B) and C) Pots were positioned outdoors during the month of June (with night and day temperatures ranging between 13.2 ± 0.6

°C and 24.3 ± 0.7 °C). The substrate consisted of B) 1:1 clay-loam:perlite mixture; B) 1:1 Pro-Mix:sand mixture. Different letters denote significant differences amongst treatment groups (n = 10 for each treatment, with error bars denoting standard deviation).

In an outdoor common garden experiment, we examined whether substrates with contrasting nutrient retention and drainage characteristics (i.e. a 1:1 clay-loam soil:perlite mixture or a 1:1 Pro-Mix BX growing medium to sand mixture) would alter the effectiveness of the coated urea pellets for promoting plant growth. Clay-loam soil has a high cation exchange capacity and low drainage compared to low-quality sandy-loam soil, because sand has comparatively weak nutrient and moisture retention properties.⁵⁰ Plant growth was compared in the two soil types in response to the fertilization treatments described above or no fertilization. For the clay-loam and perlite mix, uncoated urea addition resulted in more than a doubling in aboveground biomass relative to the no fertilization control, and all of the coated urea pellets resulted in approximately triple the aboveground biomass (Figure 8B). For the Pro-mix and sand mixture, the plant growth response did not vary significantly among the no fertilization and uncoated control. Unexpectedly, biomass was lowest for the ESN and hand-coated pellet treatments (Figure 8C).

Overall, PEtG coated pellets behaved at least as well as commercially available ESN slow release fertilizer in terms of promoting plant growth, although there was variation in their effectiveness based on the substrate type examined. Further nutrient release studies would be needed to optimize coating thickness and release rates in the field. However, our results provide a positive step for the development of the first SIP fertilizer coating that can increase nutrient synchronization while also reducing microplastic accumulation in soil systems.

Supporting information

476 Root-zone acidification, additional SEM images, cross-sectional images of coated urea pellets,
477 experiments to determine the optimal nitrogen application rate, belowground biomass data.

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481 **Notes**

482 Gillies and Fan declare that they are co-inventors on a patent on polyglyoxylates.

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