Organic & Biomolecular Chemistry

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Sulfur Polymer Composites as Controlled-Release Fertilisers

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Sulfur polymer composites were prepared by the reaction of canola oil and elemental sulfur in the presence of the NPK fertliser components ammonium sulfate, calcium hydrogen phosphate, and potassium chloride. These composites released nutrients in a controlled fashion, resulting in less wasted fertiliser and better health for potted tomato plants when compared to free NPK.

Introduction

Fertilisers are critical for producing sufficient food for a global population predicted to approach 10 billion by 2055.[1] Because increasing fertiliser costs can lead to food shortages,[2, 3] it is critical to conserve these resources—especially when global fertiliser demand is only expected to increase.[2, 4] The conservation of phosphorous nutrients is especially important, as a sustainable supply of mineral phosphorous is not guaranteed.[3] This resource problem is compounded by the loss of fertiliser through leaching, tailwater runoff, and volatilisation.[5] By some estimates, more than 50% of fertilisers applied to crops are not used by the plant.[6, 7] This fertiliser loss is not only a waste of material and economic resources, but it also leads to ecological harm through water eutrophication.[5, 8]

One strategy to prevent fertiliser loss is to use slow- or controlled-release fertilisers.[2, 5, 7, 8] These formulations typically feature a semi-soluble or complex form of the nutrient (such as urea-formaldehyde polymers and high molecular weight polyphosphates) or a coated fertiliser in which the nutrient diffuses through a permeable or semi-permeable barrier. In some cases, the coating is degradable, which facilitates nutrient release.[5, 8]

For coated or encapsulated fertilisers, the barrier can be an organic or inorganic material. Synthetic polymers such as polyurethanes and polyolefins have been explored as organic NPK coatings, as have natural biopolymers such as lignin, starch, and cellulose.[5, 8] Inorganic coatings are typically comprised of silicates, phosphates, or sulfur.[8] While these strategies and formulations for slow-release fertilisers are promising, they suffer from a number of limitations that restrict industrial uptake. For instance, synthetic polymer coatings are not always biodegradable and persist in the environment.[8] Natural polymers such as lignin, starch and cellulose, while abundant and degradable, are often too hydrophilic to control water permeability and nutrient leaching.[5] Inorganic coatings and composites are often brittle, resulting in fractures that make the release profile difficult to control.[5] When these limitations are considered with the high cost of production, it is not surprising that <1% of all NPK fertiliser is applied as a slow- or controlled-release formulation.[7]

Our interest in attempting to overcome these obstacles was motivated by the many potential benefits of economical slow-release fertilisers: lower nutrient waste, reduced impact on the environment, the prospect for synchronising release to plant need, and enhancing crop yields to feed a growing population.[2, 5, 7, 8] We were also inspired by extensive efforts over the last 50 years to use sulfur coated urea and other sulfur composites as slow-release fertilisers,[5, 8] including dedicated steps toward industrial production.[9] The main shortcoming for sulfur-coated fertilisers is still the brittle nature of the elemental sulfur and its tendency to fracture.[5, 8] Nevertheless, sulfur is inexpensive, highly abundant, a secondary plant nutrient, and a fungicide.[5] We were therefore curious to test if sulfur could be converted into a more durable polymer to encapsulate fertiliser or form a composite with NPK nutrients for slow- or controlled-release.

Since the introduction of *inverse vulcanisation* by Pyun and collaborators in 2013,[10] there has been a growing interest in making polymers and related materials from elemental

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sulfur.[11-13] In the inverse vulcanisation reaction, molten sulfur is heated above its floor temperature to provoke ring-opening polymerisation. The thiyl radicals at the ends of the resulting polysulfide chains can then react with an unsaturated small-molecule cross-linker—typically an alkene, polyene or alkyne.[12] Termination, for instance by radical recombination, provides a stable polysulfide polymer. These materials typically contain 50-90% sulfur by mass, which imparts many intriguing chemical, mechanical and optical properties.[11-13] These high sulfur materials have been tested as electrodes for Li-S batteries,[10, 14-26] infrared transparent lenses for thermal imaging,[27-29] repairable and dynamic materials,[27, 30-32] sorbents for heavy metals[31, 33-42] and oil-spill remediation,[43] precursors to functional and porous carbons,[44, 45] porous materials for CO_2 capture,[46] antibacterial surfaces,[47] photoactive materials and catalysts,[48, 49] and thermal insulation.[41] In many cases, these studies have featured the deliberate use of renewable and inexpensive organic cross-linkers, to help facilitate up-scaling and sustainability.[18, 26, 31, 33-38, 40, 43, 50-52]

In this study, we use an unsaturated triglyceride (canola oil) as a cross-linker in inverse vulcanisation to form a polysulfide polymer that encapsulates NPK nutrients. We have previously explored this material in mercury sorption,[36, 53] water purification,[40] and oil spill remediation[43] and related materials have been tested in electrochemical applications.[52] Here we present a new application of this material as a key component of slow-release fertilisers. We were intrigued by the prospect of converting the sulfur into a polymer barrier for NPK release, and the possibility for the sulfur in the polymer, or unreacted free sulfur, to be available as a secondary nutrient. Moreover, this canola oil polysulfide can be made from recycled cooking oil,[36, 43] so there is an opportunity to contribute to the circular economy in converting this food waste into fertiliser for crops.[54, 55]

Results and Discussion

The fertiliser composites were first prepared by reacting an equal mass of canola oil and sulfur in the presence of the NPK components ammonium sulfate, calcium hydrogen phosphate, and potassium chloride (Figure 1).
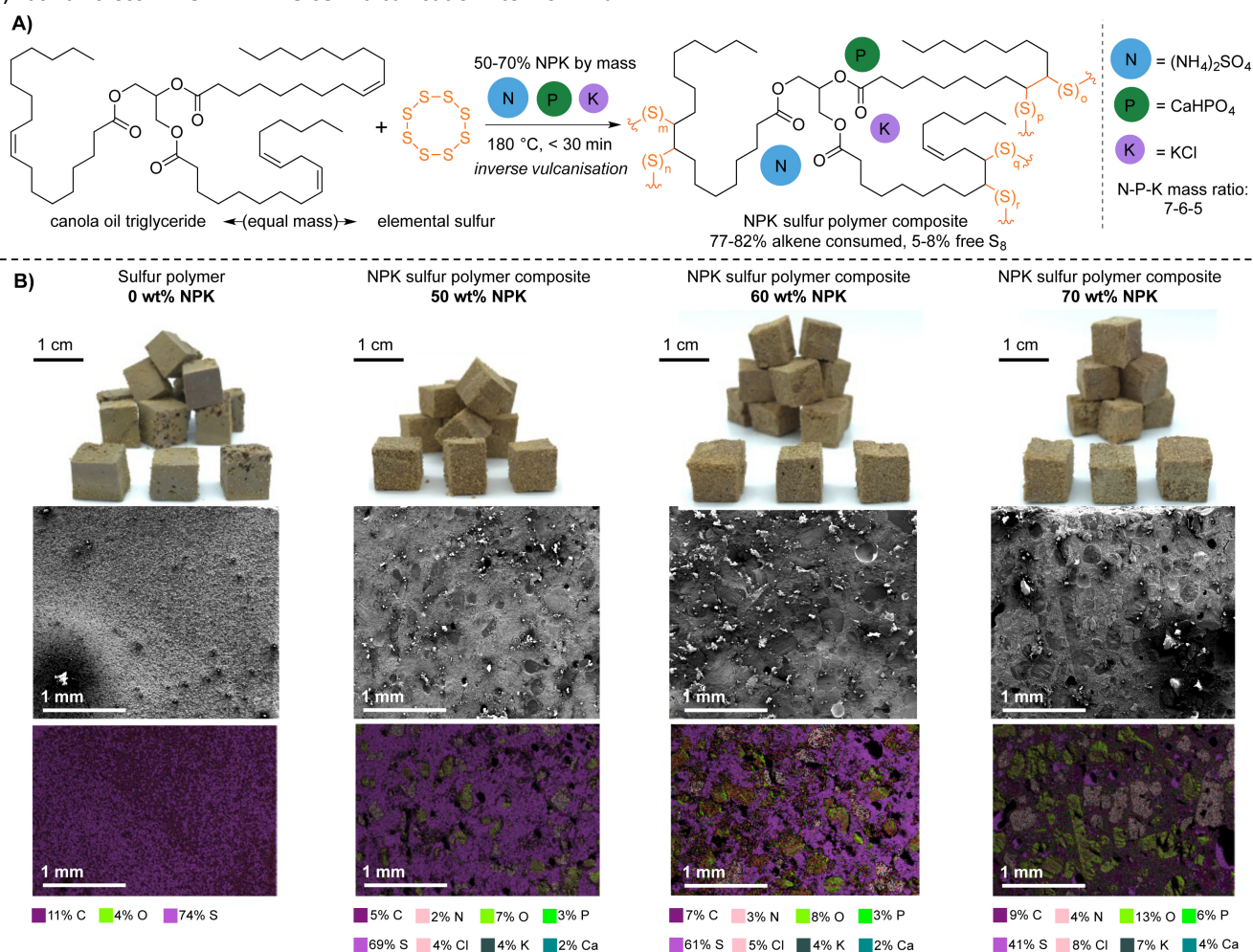

Figure 1: A) A sulfur polymer composite was prepared by the reaction of sulfur and canola oil in the presence of an NPK nutrient mixture. B) Digital images, SEM micrographs and EDX elemental mapping of the NPK sulfur polymer composites.

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The mass ratio of the nutrients was fixed at 7 $(NH_4)_2SO_4$: 6 $CaHPO_4$: 5 KCl, based on common commercial NPK formulations. The amount of NPK and polymer in each composite was varied so that the final product contained 50%, 60% or 70% total NPK by mass. For instance, a 200 g batch of composite containing 50% NPK was prepared by first adding sulfur (50 g), canola oil (50 g), and the 7-6-5 NPK mixture (100 g) to a 300 mL reactor equipped with an overhead stirrer. The mixture was set to heat to 180 °C with gentle stirring (10 rpm, 7 cm impeller width). After the sulfur melted (~120 °C), the stirring was increased to 120 rpm to ensure efficient mixing. The reaction was stopped after 30 minutes total reaction time, which coincides with an increase in the viscosity of the mixture. Upon cooling, the sulfur polymer composite appears as a brown solid. The composite was then cut out of the reactor into cubes (0.5 cm, 1.0 cm, or 1.5 cm) (Figure 1 and S4-S5).

The composites were first characterised by ^{1}H NMR spectroscopy in pyridine-D_5. Typically ~80% of the alkenes in the triglyceride were consumed through the reaction with sulfur for the NPK composites, as determined by the relative integration of the alkene signals and the signals for the methyl groups at the end of the fatty acid chain (S8-S10). The ^{1}H NMR spectra were essentially the same for the 50%, 60% and 70% NPK composites, indicating the amount of NPK did not appear to influence the chemical structure of the sulfur polymer. IR spectroscopic analysis revealed the expected signals for a polymer made from a triglyceride, including the strong C=O stretch of the esters at 1745 cm^{-1} (S11). Quantitative differential scanning calorimetry (DSC) was used to determine the amount of free elemental sulfur in each composite, with 6-8% of the mass of the composite presenting as free sulfur (S11-S12). Finally, imaging using a scanning electron microscope (SEM) and energy-dispersive X-ray spectroscopy (EDX) revealed a sulfur polymer network embedded with ammonium sulfate and potassium chloride crystals, as well as free sulfur particles (Figure 1B and S13-S17). The calcium hydrogen phosphate was dispersed evenly through the polymer matrix, as it was added to the reaction in powdered form. The SEM micrographs and EDX images are shown in Figure 1 for all fertiliser formulations, including a control sample of sulfur polymer prepared without the addition of the NPK salts.

After establishing that sulfur can react with canola oil and form a polymer in the presence of the NPK salts, the elution profiles of the composites were assessed in soil columns. First, 2 kg of potting soil was washed by soaking it in 5 L of deionised water for 1 hour, and then filtering to remove the salts, nutrients and other water-soluble components. This washing procedure was repeated six times, so that the water outlfow had a constant conductivity of less than 100 μS. To prepare the column, 150 g of the washed soil was added to a 300 mm PVC tube with a mesh barrier at one end (Figure 2A and S18). The soil was wetted and packed by adding 100 mL deionised water to the column. Next, 50 mL of water was added to the column and the outflow was collected for 3 minutes to determine the conductivity of the outflow before the fertliser was added

(typically 80-100 μS). NPK composites (50%, 60% and 70% NPK), the canola oil polysulfide (0% NPK), and free NPK salts were then added to separate soil columns at a 5 cm depth (Figure 2A and S18) For the polymer and composite samples, cubes of 0.5 cm, 1.0 cm, and 1.5 cm dimensions were tested. All columns with an NPK component had the same mass of total nutrients (2.9 g NPK). To elute the NPK, 50 mL of deionised water was added to each tube and the conductivity of the outflow was measured after 3 minutes of elution. After this period, an additional 50 mL of deionised water was added to the column and the conductivity of the outflow was monitored again. This process was repeated until the conductivity was constant and below the initial measurement. At this point, the column was incubated for two days and the elution profile repeated. Four total elution profiles were assessed for each sample, with a 2 day incubation perdiod between each of these elutions.

The conductivity of the outflow for each sample is plotted in Figure 2. The elution profile for the column containing the free NPK reveals that the nutrient salts are rapidly dissolved and washed off of the column—most in the first elution (Figure 3B). This result illustrates how unencapsulated NPK can be easily washed off of soil and lost in tailwater. The high conductivity in the first elution—an average of 14053 μS after a mere 150 mL of water for triplicate experiments—also illustrates that there is a risk that the NPK concentration available to a plant may be too high and lead to nutrient burn (*vide infra*). Eluting at days 3, 5, and 7 resulted in low conductivity in the outflow, because most NPK was lost in the first elution. In contrast, the NPK encapsulated in the sulfur polymer exhibited controlled release (Figure 2C-D). At the beginning of each elution, the outflow would increase to a maximum conductivity that was an order of magnitude smaller than the outflow for the free NPK, before returning to an outflow conductivity of <100 μS. For the first elution, the released NPK is likely that on or near the surface of the sulfur polymer composite. Importantly, extended elution with water did *not* lead to more NPK release in the first elution. Rather, there is a lag time required for the water to enter the sulfur polymer composite, dissolve the NPK nutrients, and leach them into the outflow. This is an important finding because it means that excess irrigation or rainwater would not necessarily release more NPK from the composite. Subsequent elution at days 3, 5, and 7 showed a similar profile (Figure 2D-F). Both the size of the NPK sulfur polymer composite and the amount of NPK by mass influenced the release profile. Smaller NPK composites, with higher surface area, release more NPK with each elution. With increasing NPK in the composite, the rate of release is higher. Together, these parameters could be used to tune the NPK release.

In a similar elution experiment with the sulfur polymer and no NPK, the outflow had negligible conductivity (Figure 2C). This means changes in conductivity for the NPK samples can be attributed to the release of the fertiliser salts. Ion chromatography of the outflow for the NPK sulfur polymer composites also confirmed that the conductivity did indeed arise from the release of ammonium sulfate, calcium hydrogen

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phosphate and potassium chloride (S21). Finally, we attribute the release mechanism to dissolution and diffusion of the NPK solution from the polymer to the bulk water through channels in the polymer. The NPK does not appear to diffuse through the bulk polymer, as a 1 mm sulfur polymer membrane

separating a solution of 1000 ppm KCl and deionised water did not result in ion migration through the polymer over the course of 7 days (S22).
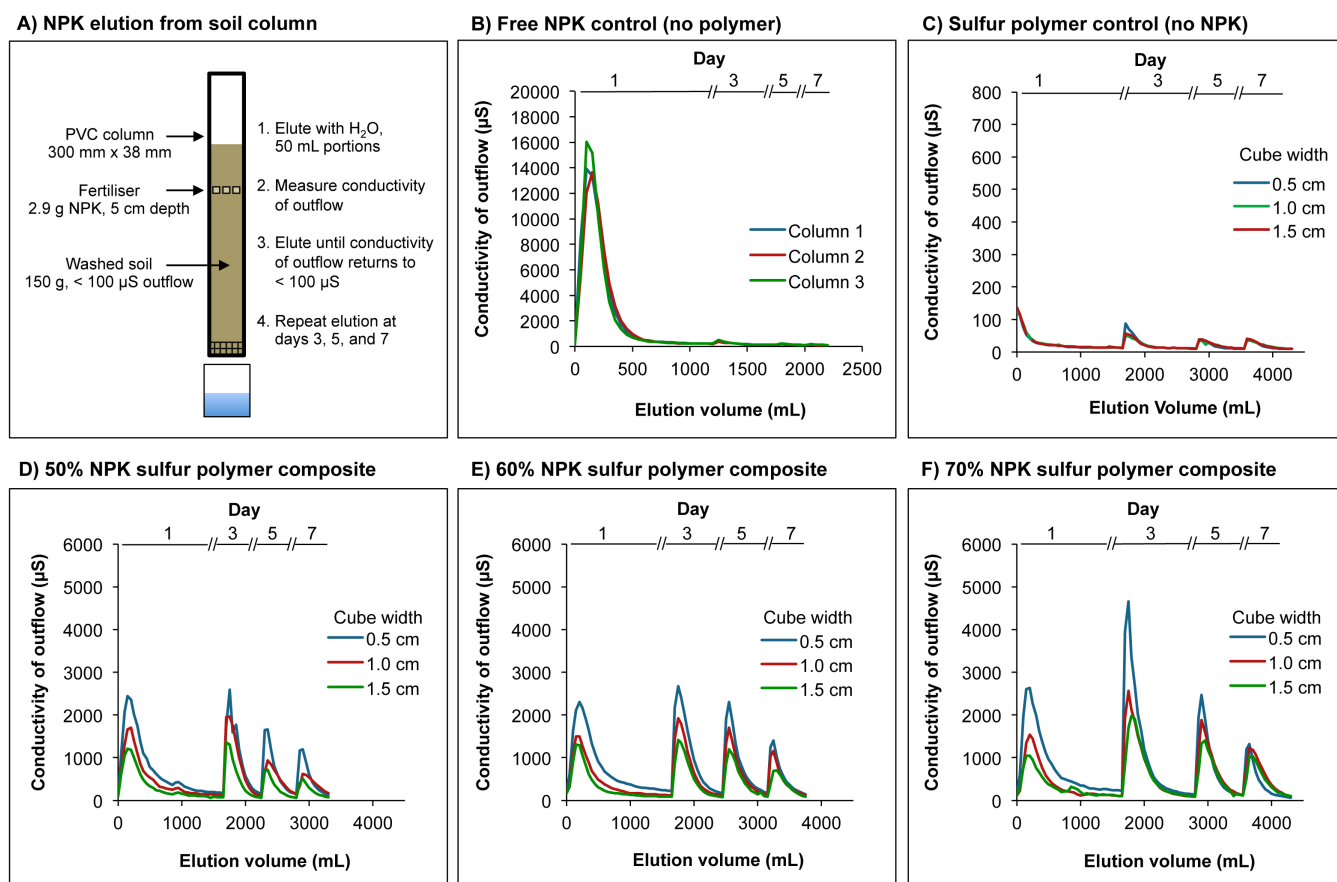

Figure 2: A) Elution study in which fertiliser is placed in a soil column and the conductivity of the outflow is measured. The conductivity is directly related to NPK dissolution and elution from the column. B) Free, unbound NPK is washed from the column, with most nutrients lost in the first 500 mL of water. C) The conductivity of the outflow for a column containing the sulfur polymer but no NPK salts is negligible. D-F) Sulfur polymer composites containing 50%, 60% or 70% NPK release nutrients in a controlled manner. The water releases a portion of the NPK with each elution, with a lag time required to leach additional nutrients from the polymer.

Motivated by these release profiles, we next initiated a small-scale plant growth study to establish whether the NPK composites could benefit food crops. We selected potted tomato plants (*Lycopersicom esculentum*) as a useful model because of their rapid growth and high NPK nutrient demand. The roots of 12 young plants (< 20 cm height) were washed to remove soil and bound nutrients before transplanting to nutrient-poor soil (S23). As in the column studies, this soil was washed thoroughly so the conductivity of the outflow was < 100 μS. The experiment featured four groups, with three plants in each group: (A) a negative control group with no polymer and no NPK; (B) a negative control group with polymer, but no NPK; (C) the experimental group with the 60% NPK sulfur polymer composite (1 cm cubes); (D) the positive control with free NPK. In groups C and D, the total amount of NPK was the same (5 g). The polymer, NPK sulfur polymer composite, or free NPK were buried in the soil at a 2 cm depth.

The plants were exposed to light for 10 hours per day, using a 600 W high-pressure sodium lamp equipped with a timer. For the first five weeks, the plants were watered three times per week, with 200 mL of water. The conductivity of the tailwater was measured after watering the plants. After five weeks, the amount of water was increased to 2 x 200 mL each day, for five days a week to meet increasing nutrient and moisture demands as the plants grew (See S23-S24 for additional details).

As seen in Figure 3, over the first three weeks of growth, the plants treated with the controlled release NPK sulfur polymer composites were the healthiest (Figure 3, Group C). The negative control groups without NPK were yellow and shorter, as expected with no nutrients available (Groups A and B). Remarkably, the plants with the free NPK (Group D) fared poorly, with severe nutrient burn (Figure 3, Day 21). This is a consequence of having too much free NPK available to the plant. This result also highlights one of the advantages of slow- and controlled-release fertilisers.

The plant growth and tailwater conductivity was monitored for 10 weeks, over which time it was clear that the plants treated with the controlled-release NPK sulfur polymer composite (Group C) were significantly greener, taller, and grew more fruit than the other groups (Figure 3 and S24-S36). The conductivity of the tailwater, also analysed by ion chromatography (S37), clearly showed that the controlled-release fertiliser resulted in less wasted nutrients—another important advantage for slow- and controlled-release NPK formulations over free NPK.

These preliminary growth studies are a promising foundation for larger greenhouse studies in the future. We are also investigating the fate of the sulfur polymer and whether it can decompose in soil and how the products of (bio)degredation affect soil structure and plant health. Preliminary experiments indicate that the triglyceride backbone of the polymer can indeed hydrolyse slowly in basic water and release glycerol (S38), so it is chemically feasible for this to occur. Future studies will establish the rate of this process in soil and the extent to which soil microbes hydrolyse the esters or reduce the polysulfides in this polymer. Understanding these degradation pathways is important not only for more general use in fertiliser applications but also for any application in which these sulfur polymers are used in the environment. The results of these studies will be reported in due course.
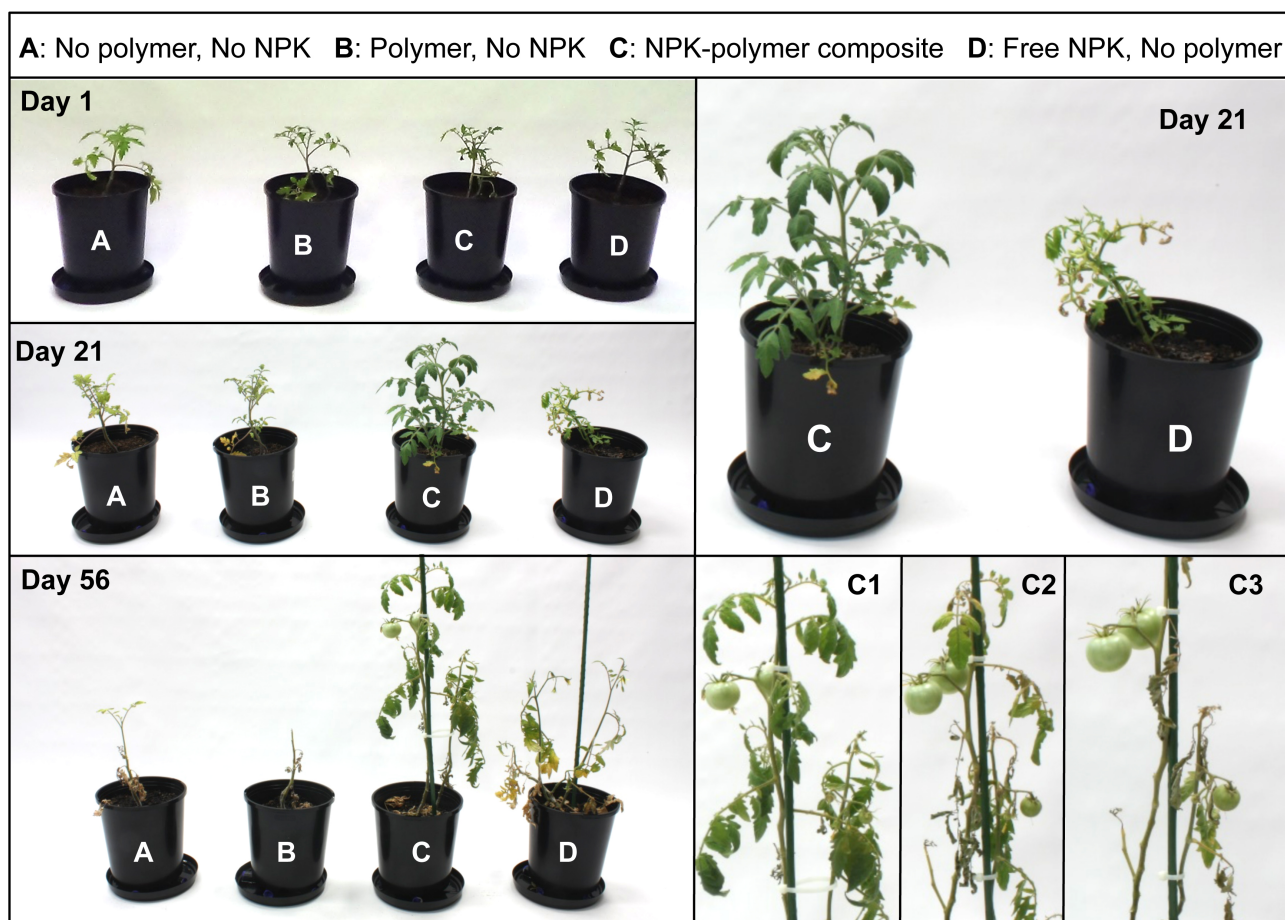

Figure 3: Day 1: transplanted tomato plants. Day 21: The controlled-release NPK sulfur polymer composite produced consistently green and healthy plants (Group C) while the plants with the free NPK suffered from nutrient burn. Day 56: The controlled-release NPK sulfur polymer composite promoted more rapid growth and more fruit than the plants with free NPK. Plants C1, C2 and C3 are the three different plants grown for 56 days with the NPK sulfur polymer composite. For additional images of the plants in this study, see the supplementary information (S24-S36).

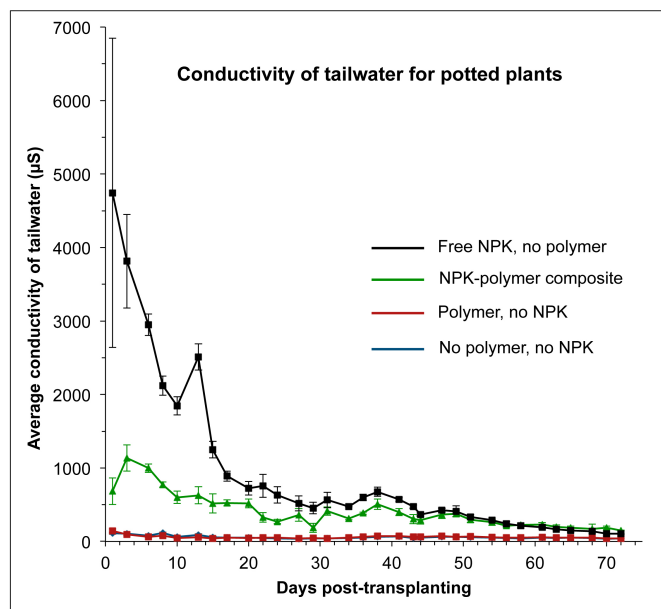# Organic & Biomolecular Chemistry

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Figure 4: The conductivity of the tailwater for the potted tomato plants in Figure 3. The higher conductivity for the free NPK indicates that more nutrients are lost in tailwater compared to the controlled release of the NPK sulfur polymer composite.

Conclusions

Inverse vulcanisation was used to prepare a sulfur polymer composite useful in the slow-release of NPK fertiliser. The nutrients are released after water slowly dissolves and leaches the inorganic components from the polymer. The diffusion of nutrients from the composite features a lag period that is critical in preventing excessive nutrient release with prolonged irrigation. The nutrient release can also be controlled, in part, through the size of the fertiliser particles and the total amount of NPK in the composite. In growth studies for potted plants, the slow-release composite prevented nutrient burn and fertiliser loss in tailwater, when compared to free NPK. Because the featured polymer is made from sulfur and canola oil, the feedstocks are abundant and inexpensive. Notably, the same polymer can also be made from used cooking oil,[36, 40, 43] which means there is an intriguing prospect of establishing a circular economy in which canola oil is produced in the agriculture sector, used as food, and then recycled to produce fertiliser for food crops.

Future studies will focus on the long-term (bio)degradation of the canola oil polysulfide and its effects on soil structure and the wider environment. Expanded growth trials are also envisioned with a wider panel of food crops. These studies will help clarify the prospects of sulfur polymers as new class of slow- and controlled-release fertilisers and their potential to help meet the global challenge of sustainable food production.

Experimental Details

Full experimental details, including spectroscopic data and material characterisation, expanded details on growth studies, and additional images of plants are included in the Electronic Supplementary Information.

Acknowledgments

Conflicts of interest

Two authors, J.M.C. and M.J.H.W., are inventors on a patent application that includes, among its claims, the synthesis and applications of the canola oil polysulfide featured in this study: WO2017181217; Priority Application AU2016-901470, April 20 2016.

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