Development of Novel Polymeric Materials for Agroprocess Intensification

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ABSTRACT: The potential uses of hydrophilic nanostructured microporous polymers (PolyHIPE polymers) in agriculture were investigated with rye grass as a model plant. The basic material was crosslinked styrene–divinyl benzene polymer with a 90 vol % porosity. They were microwave-sulfonated to obtain hydrophilic polymers with water adsorption capacities of 10-fold and 18-fold with nominal pore sizes of 20 and 150 μm, respectively. The small-pore-size PolyHIPE polymer was rigid, whereas the large-pore-size polymer was spongy and adsorbed water rapidly. When this spongy polymer was used as a soil additive at 0.5 wt % with increasing water stress (normal, semiarid, and arid conditions), the dry biomass yield increased by about 30, 140, and 300%, respectively, after 21 days of cultivation compared with the control, which contained no sulfonated spongy PolyHIPE polymer. The rigid sulfonated PolyHIPE polymer did not show any statistically significant effect on the biomass yield. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 3292–3299, 2010

Key words: biological applications of polymers; functionalization of polymers; microstructure; swelling; synthesis

INTRODUCTION

Superabsorbent polymers (SAPs) and hydrogels have considerable potential for a wide range of uses, such as in medicine release systems, sanitation, and personal hygiene products and for agricultural and horticultural applications. In agricultural applications,[1,2] the greatest potential use of SAPs is in the soils with low water-holding capacities and in semiarid countries where the irrigation of crops is carried out with low-quality water, which exacerbates the soil salinity. Hydrogel polymers have previously been shown to improve growth under saline conditions by reducing the availability and uptake of both Na$^+$ and Cl$^-$ ions. Water-deficit stress is a common problem for many agricultural and forestry crops and is due to drought, salinity, or temperature; it occurs when the demand for water by the plant exceeds the available supply.[3] SAPs and hydrogels have been reported to absorb up to 2400 times their weight in water,[4] which can be retained even under pressure. However, this water-holding capacity is reduced drastically in the presence of electrolytes, and because of poor crosslinking, such polymers are readily degraded and washed away.

The effect of a hydrogel or SAP on soil water retention depends on the type and amount used (usually between 0.25 and 1 wt % polymer in the soil); generally, the lower the SAP particle size, the more water is absorbed and at a faster rate.[5] The application of agricultural polymers and hydrogels has been shown to supply water to growing crops, reduce the impact of water-deficit stress, reduce irrigation requirements, lower the death rate of plants, improve fertilizer retention in soils, and increase plant growth.[6] Plant growth benefits, including plant height, leaf width, total dry weight, and increased length of time before the plant begins to wilt, have been observed.[7] This is achieved via the influence of the polymer or hydrogel on the soil permeability, density, structure, texture, compaction, aeration, erosion, and microbial activity and through effects on the water runoff, evaporation, and infiltration rates.[7] Polymers and hydrogels have been shown to

improve the soil density, structure, texture, and so on in some soils, and systems containing just 0.5 wt % polymer have been shown to transform loose sand into a solid material, with significant reductions in hydraulic conductivity.[8]

Recently, we showed that a new class of nanostructured microporous (NSMP) polymers offer several advantages over SAPs and hydrogels as soil additives in enhancing plant growth and crop yield.[9] These advantages include the cost, controlled size of the soil additive, pore microstructure (i.e., pore and interconnect size, pore volume, and pore wall chemistry), ability to include biologically or chemically active components (e.g., bacteria or fertilizer), control of rigidity, and water adsorption capacity. These NSMP polymers are generically known as *hydrophilic nanostructured microporous polymers* (PolyHIPE polymers or PHPs) and are formed with a high internal phase emulsion (HIPE) polymerization route.[10–14] PHPs can be either hydrophilic or hydrophobic or indeed biphylic and have a well-defined pore microstructure. These materials are used in process intensification;[12] including bioprocess intensification and tissue engineering, where the control of the surface properties and pore structure is essential.[11,12,14–17] It has been shown that the behavior of microorganisms (bacteria or mammalian cells) is dependent on the size of the microenvironment in which they are confined. The microenvironment facilitates the interactions between microorganism and leads to bioprocess intensification.[12]

In this study, we examined the performance of hydrophilic, elastic, ionic NSMP polymers as soil additives in the enhancement of biomass growth, principally under water stress, which is important in the supply of biomass for biomass-based sustainable energy technology (see, e.g., Ashraf et al.[18]). This process can be described as agroprocess intensification, as the underlying principles of the enhancement/intensification in this case were similar to those encountered in bioprocess and chemical process intensification.[9]

EXPERIMENTAL

Materials

Styrene, divinyl benzene (DVB), potassium persulfate, and sorbitan monooleate (Span 80) were purchased from Sigma Aldrich (Gillingham, UK) and were used as received. John Innes Loam-Based Compost No. 3 was used for the soil. Horticultural sand was supplied by Moorbank Gardens (Newcastle, United Kingdom). The perennial rye grass used was of the Superstar variety and was purchased as seeds from the Agriculture, Environment, and Fisheries Department (London, UK).

Characterization

Scanning electron microscopy (SEM)

SEM studies were conducted with a Hitachi FEI XL30 environmental scanning electron microscope (ESEM) FEG machine. The fracture surfaces of the samples were gold-coated before SEM examination (Newcastle University, UK). We measured the pore size by measuring the pore diameter on the SEM micrographs and recording the number-average size after correcting them to take into account the random nature of the fracture surface.[16]

Surface area analysis

PHPs of various thicknesses were washed and dried, and then, Brunauer–Emmett–Teller surface area measurements were carried out with a Beckman Coulter SA310Plus Brunauer–Emmett–Teller gas adsorption surface area analyzer (Palo Alto, CA).

Water uptake

The water adsorption capacity of the polymers was determined with sample disks 24 mm in diameter and 4 mm thick; these were fully dried before immersion into deionized water at room temperature for 30 s. They were then removed from the water, dabbed dry with tissue paper to remove water from the surface, and reweighed to determine the water adsorption:

$$\text{Water adsorption capacity} = (W_s - W_d)/W_d$$

where W_s and W_d are the weights of the soaked and dry PHPs, respectively.

Planting, watering, and harvesting

Horticultural soil was mixed with 25% horticultural sand, and 200 g of the resulting mixture of soil was placed into 8 cm diameter pots. The soil was 6 cm deep in the pot and reached the lower lip of the pot, where the diameter was 7 cm, and the surface area was 38.5 cm^2 and was 1.5 cm below the upper lid of the pot. Polymer particles (0.5 wt %) were thoroughly mixed into the soil before the addition of 5 g of perennial rye grass seed which was spread evenly over the soil surface. A control treatment without polymer was also used. The seeds were covered with a thin layer of soil until the soil was level with the lower lip of the pot and were then watered.

Three different watering schedules were used for grass growth: (1) daily watering (a normal regimen where the felt matt on which the pots stood was kept moist throughout the day with tap water), (2) weekly watering (semiarid conditions, 40 mL of

water per pot), and (3) reduced weekly watering (arid conditions, 20 mL of water per pot).

The pots were randomly distributed within a 2 × 2 m² area of greenhouse. Dishes prevented water from reaching the droughted pots. After 21 days, the grass was cut at the upper lip level of the pot, 1.5 cm above the soil surface. The grass was then immediately weighed to determine the fresh weight before it was placed in an oven at 60°C for 72 h and reweighed to determine the dry weight.

Preparation of the PHPs

The PHPs used in these experiments consisted of 90% void and 10% polymer phase by volume. They were prepared by the technique described by Akay and coworkers.[10,12,13] The preparation was divided into three stages: (1) HIPE formation, (2) polymerization of HIPE to obtain the PHPs, and (3) functionalization (sulfonation) of the PHPs.

HIPE formation

The aqueous phase of the emulsion (90 vol %) consisted of deionized water, an initiator of polymerization (potassium persulfate), and 5% sulfuric acid. The oil phase (10 vol % of the total emulsion) consisted of a monomer (styrene), nonionic surfactant, sorbitan monooleate (Span 80), and the crosslinking agent DVB. The oil phase composition consisted of styrene ($86 - X$ wt %), Span 80 (14 wt %), and DVB (X wt %). In the experiments, the concentrations of styrene and DVB was changed in the range $2 < X < 10$ wt % to optimize the properties of the PHPs with respect to the water adsorption and mechanical characteristics.

In line with the emulsification method developed by Akay and coworkers,[10,12–14] the oil phase was placed into the mixing vessel (internal diameter = 12 cm) first, and then, the aqueous phase was dosed into the oil phase via a peristaltic pump while mixing occurred. Mixing was achieved via three flat paddles (9 cm in diameter) stacked at right angles as close to the bottom of the vessel as possible.

The control of the pore and interconnect sizes in the microporous polymer was achieved mainly through the control of the emulsion oil phase composition, temperature of emulsification, mixing speed, rate of internal phase dosing, and total mixing time. Two types of PHPs were compared in this study: a rigid polymer and a spongy polymer. Although the compositions of the oil phase were identical, the elasticity of the sulfonated PHPs was dictated by the pore size of the PHPs, which in turn, could be controlled by the mixing time and temperature of emulsification. For the rigid polymers, the aqueous phase was dosed into the oil phase with continuous mixing for 10 min; this was followed by a further 30 min of mixing with the impeller set to a mixing speed of 300 rpm throughout. For the more spongy polymers (with large pore size), the dosing time was reduced to 5 min, and the subsequent mixing (homogenization) time was reduced to 1 min at the same mixing speed at 300 rpm throughout.

Polymerization

HIPEs were transferred to plastic containers and sealed for polymerization at 60°C for 8 h in a preheated oven. During polymerization, some coalescence of the dispersed phase droplets could take place because of the presence of acid in the dispersed phase; this resulted in the formation of very large (several hundred micrometers in diameter) coalescence pores dispersed into the primary pores after polymerization.[13,14]

Functionalization (sulfonation and neutralization)

After polymerization, the PHPs were cut into 0.4 cm thick disks and dried in the air in a fume cupboard to allow an 80% weight reduction through the evaporation of water. Sulfonation of these disks was be carried out with microwave irradiation[19] followed by neutralization with ammonium hydroxide. Although in practical applications, this would be an economically viable route, in this study, we soaked the PHP disks in 97% sulfuric acid for 2 h followed by pulsed microwave irradiation (30 s of irradiation and 2 min of relaxation and the reversal of the disk surfaces) until the total irradiation time for 14 disks was typically 240 s for the polymer and 150 s for the spongy polymer, by which time, the latter had swollen into a soft, spongy structure. These PHP disks were then washed in water and then neutralized with ammonium hydroxide; this was followed by washing and drying.

Statistical analysis of plant yield data

The mean fresh and dry weights for each harvest were plotted into bar charts. The mean yields were compared with two sample t tests of independence with equal variance assumed at 95% confidence and were confirmed with a one-way analysis of variance with a Tukey's pairwise comparison.

RESULTS AND DISCUSSION

SEM

SEM analysis (Fig. 1) of the sulfonated-neutralized PHP showed that the rigid polymers had nominal primary pores with diameters of 20–50 μm, whereas
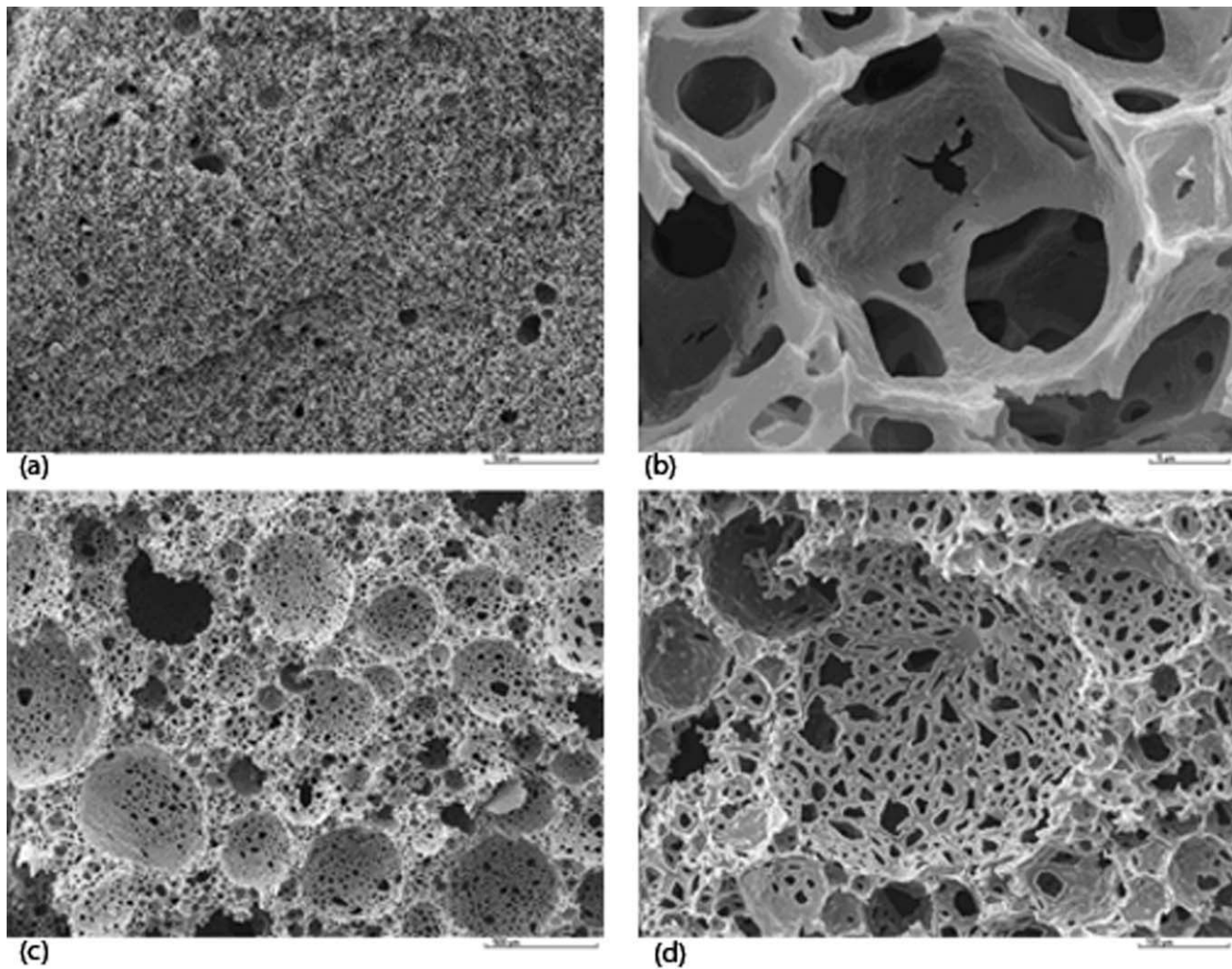
Figure 1 Structures of the (a,b) rigid and (c,d) spongy PHPs at two different magnifications. The scale bars represent (a,c) 500 and (b,d) 100 μm.

the spongy polymers had primary pores with diameters of 150–200 μm. It was clear from these micrographs that the rigid PHP did not have coalescence pores, whereas the elastic PHPs had large coalescence pores with diameters of about 500 μm. The identification and the structure of these pores were
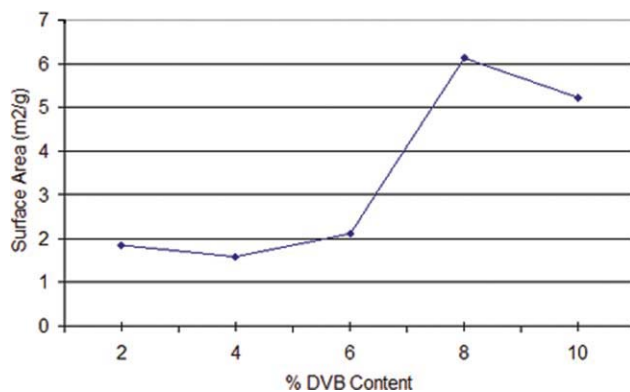

Figure 2 Effect of the DVB concentration (%) on the maximum surface area (m²/g) achieved in the polymer pores of the rigid PHP. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
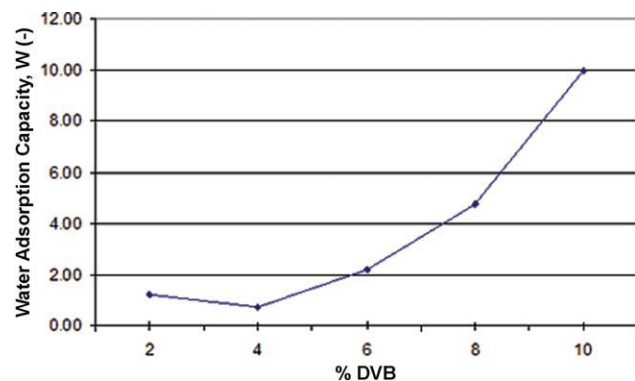

Figure 3 Effect of the DVB concentration (%) on the amount of water adsorbed by the rigid PHP. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE I
Water Adsorption Capacities, Adsorption Rates, and Surface Area Characteristics of the Rigid and Spongy PHPs

Sulfonated PHP	Relative water adsorption after 30 s	Relative equilibrium adsorption capacity	Pore size (μm)	Internal surface area (m²/g)
Rigid	7.44	9.93	20	5.2
Spongy	18.1	18.1	150	5.2

given by Akay and coworkers.[13,14] Because the wall thickness of the spongy polymer was significantly larger than that of the rigid polymer (by virtue of the pore size difference) and because the spongy PHP expanded upon water adsorption, the wall porosity of the spongy PHP was significantly higher.

Surface area analysis

DVB was used as the crosslinking agent within the polymer, and variation in the DVB content of the rigid PolyHIPE was shown to cause significant changes in the surface area of the pores (Fig. 2). A low (2–6%) DVB content resulted in a low surface area, whereas 8% DVB produced the maximum surface area that was obtained. However, the difference between the surface area at 8 and 10% was not significant. Reduced crosslinker concentration should

increase the water adsorption capacity and swelling of the polymer after sulfonation.

Structural integrity

The DVB content of the polymer was found to play a vital role in preventing the structural collapse of the rigid polymer during sulfonation, and generally, the greater the DVB content was within the polymer, the better it was at maintaining its shape during sulfonation. When DVB content was below 8%, a dramatic reduction occurred in both the surface area and the actual size of the polymer. The different polymers generally kept their circular shape after structural collapse, although the 4 and 6% DVB
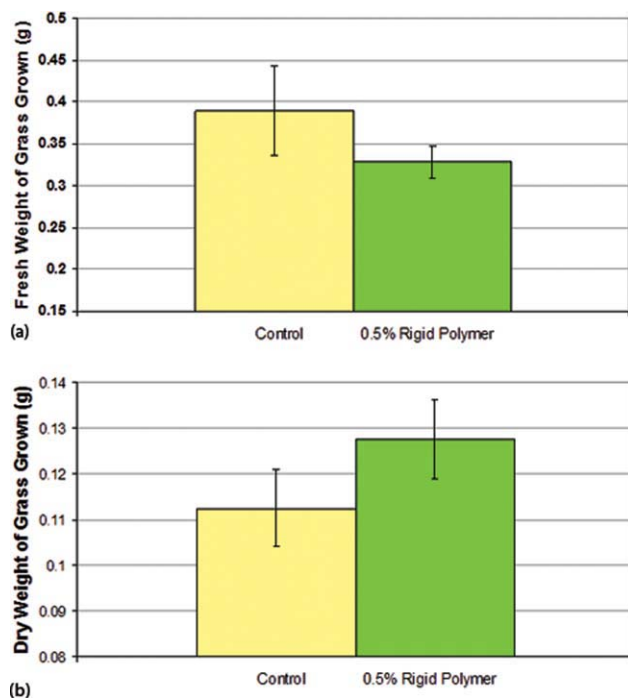
Figure 4 Effect of the rigid polymer on (a) the fresh weight yield and (b) the dry weight yield of grass grown with reduced weekly watering. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
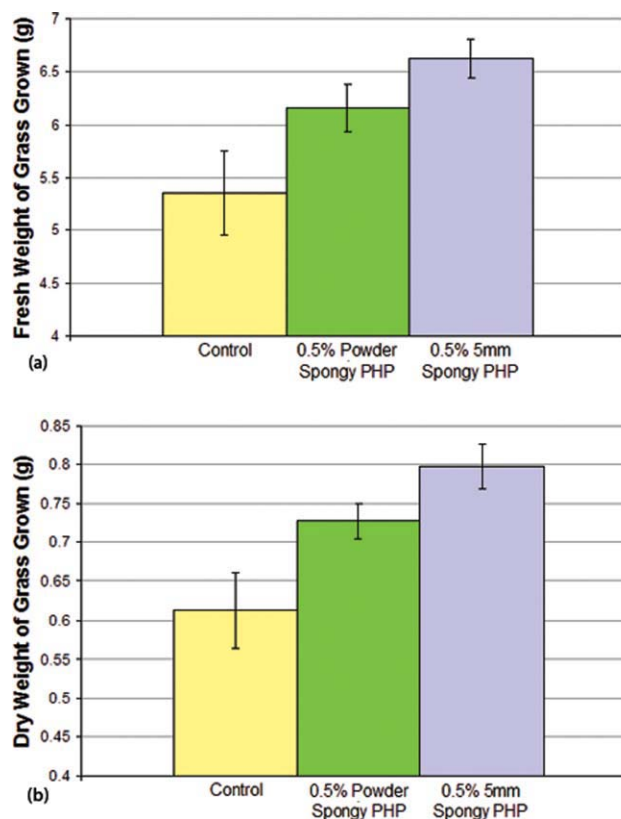
Figure 5 Effect of the spongy polymer on the (a) fresh weight yield and (b) dry weight yield of grass grown with daily watering. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
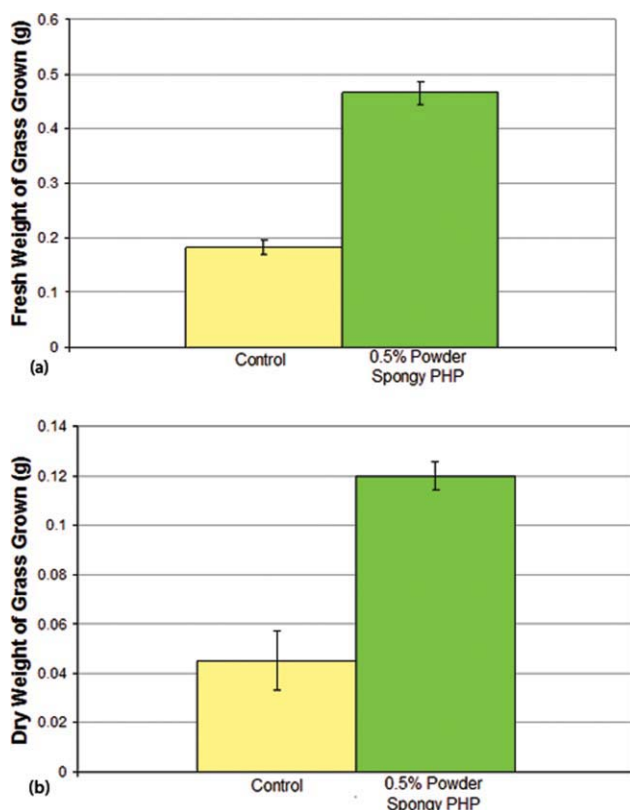
Figure 6 Effect of the spongy polymer on the (a) fresh weight yield and (b) dry weight yield of grass grown with weekly watering. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

polymers did end up slightly elliptical-shaped. At their narrowest points, it was clear that the 10 and 8% DVB polymers held their structure the best (2.5 and 2.3 cm, respectively), whereas the 6% (1.6 cm), 4% (1.4 cm), and 2% (1.6 cm) DVB polymers lost approximately a centimeter in width compared to the 10% DVB PHP.

Water adsorption

The DVB content directly affected the water adsorption of the rigid polymer (Fig. 3). Generally, as the DVB content increased, so did the maximum rate of water adsorption. A content of 6% or less DVB resulted in a very low and near constant weight increase (twofold to threefold). At 8% DVB, there was a dramatic increase in the water adsorption, and a content of 10% increased the water adsorption further still to about 10-fold; this indicated that the void volume of PHP was completely filled with water. However, because of the small pore size (ca. 20 μm), there was only slight swelling present, which limited the water uptake. Furthermore, the rate of water uptake was also relatively low; about 75% capacity was reached in 30 s.

The spongy PHP (pore size ≈ 150 μm) was produced with 10% DVB and demonstrated a maximum of about an 18-fold water-uptake capacity, which was reached within only 30 s of soaking in water. Because of these characteristics, we used 10% DVB in our experiments; this enabled us to obtain two different types of polymers at the same chemical composition. The water adsorption characteristics are shown in Table I.

Performance of the PHP as a soil conditioner

Initially, several trials were conducted with the rigid polymer to examine the effect on soil water retention on the growth of perennial grass in soil containing 25% sand. After 21 days of growth, the rigid polymer, applied at 0.5% w/w in the soil, had no beneficial affect on either the fresh or dry weight yields when compared to the control under conditions of daily watering (Fig. 4). In fact, the fresh weight in the presence of the rigid PHP was lower than that of the control.

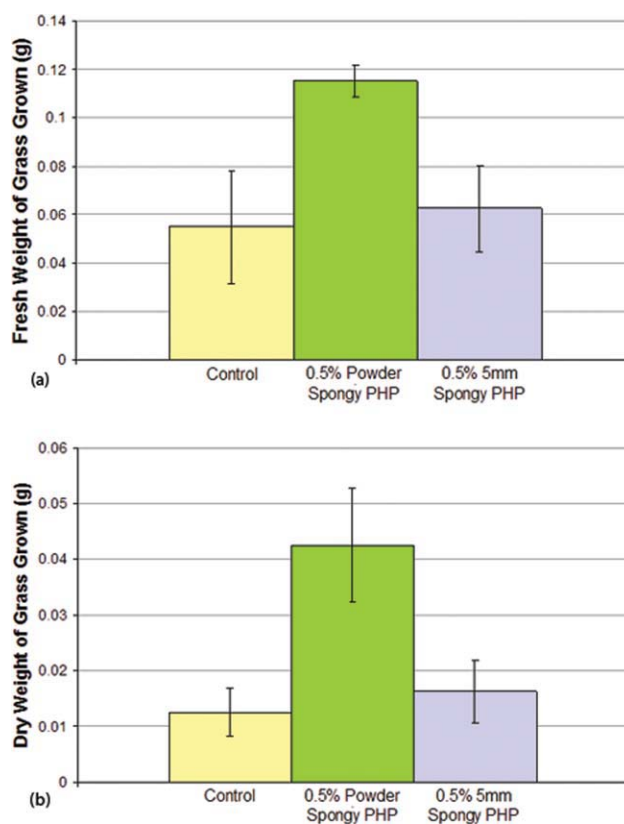Two forms of the spongy PHPs were produced, one in a powder form (particle size range = 0.1–2 mm)

Figure 7 Effect of the spongy polymer on the (a) fresh weight yield and (b) dry weight yield of grass grown with reduced weekly watering. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE II
Summary of the Results Comparing the Biomass Yield Enhancements (Fresh and Dry Biomass) Under the Three Different Watering Regimens with the Rigid and Spongy PHPs

Watering regimen	Control		Spongy PHP ($5 \times 5 \times 5$ mm^3)		Spongy PHP powder	
	Fresh weight (g)	Dry weight (g)	Fresh weight (g)	Dry weight (g)	Fresh weight (g)	Dry weight (g)
Daily watering	5.35	0.61	6.63 (+23.9%)	0.80 (+31.1%)	6.16 (+15.1%)	0.73 (+19.7%)
Weekly watering	0.18	0.05	—	—	0.47 (+161%)	0.12 (+140%)
Reduced weekly watering	0.06	0.01	0.06 (NS)	0.02 (NS)	0.12 (+100%)	0.04 (+300%)

NS indicates that the change in the yield was not significant ($p < 0.05$).

and the other in a cubical particulate (measuring ca. $5 \times 5 \times 5$ mm^3) form. Both polymer treatments were able to significantly increase ($p < 0.05$) both the fresh and dry weight yields of the grass compared with the control. The cubical particulate version was the most effective treatment for enhancing the fresh and dry weight yields under daily watering with increases of 23.9 and 31.1%, respectively, as shown in Figure 5.

Only the powder version of the spongy polymer was tested under semiarid weekly watering conditions, and it produced statistically significant ($p < 0.05$) increases in the fresh and dry weight yields of 161 and 140%, respectively (Fig. 6).

However, the powder version was the most effective treatment under arid conditions and managed to produce statistically significant ($p < 0.05$) increases in the fresh and dry weight yields of 100 and 300%, respectively (Fig. 7).

These results are summarized in Table II. Although the yield was low under arid conditions, nevertheless, the PHP soil additives did enhance the biomass yield. Various strategies to overcome salinity and water stress have been developed, including conventional breeding and molecular techniques.[18] This method is based on water management by the plant as plant roots become associated with the PHP soil additive (i.e., the roots grow preferentially through the elastic/spongy PHP) and makes the supply of water more direct. As shown by Akay and Burke,[9] plant root association can be further used in direct nutrient delivery and nitrogen fixation with bacteria within the pores of the PHP soil additive.

CONCLUSIONS

The potential uses of NSMP polymers in agriculture were investigated. The purpose of this study was to investigate the scope and mechanism of the process. Therefore, suitable symbiotic media materials were also developed to achieve a distinctive plant enhancement technique that could be rationalized within the framework of general process intensification technology. PHP is a novel microcellular polymer that can be either hydrophilic or hydrophobic, or indeed biphilic, and has a well-defined and controllable microarchitecture and water-holding capacity. The transformation of hydrophobic styrene–DVB PHP to hydrophilic form was conducted by microwave sulfonation, which was very fast compared with thermal sulfonation.[19] The rigid form (pore size = 20 μm) of sulfonated PHP had a lower water-uptake capacity (ca. 10-fold of its own weight) compared with the large-pore-size spongy form (pore size = 150 μm, water-uptake capacity = 18 fold).

The rigid sulfonated PHP treatment of soil produced no significant increase in the yield compared to the control. It was shown that the spongy sulfonated PHP treatment enhanced the yields under all of the watering regimens, especially under the semiarid and arid conditions, where the biomass yields were enhanced by about 140 and 300%, respectively, compared with the control during 21 days of growth of the perennial rye grass. Although the yield was low under arid conditions, PHP soil additives did enhance the biomass yield.

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