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Flexible polyurethane foam with sodium bentonite: Improving the properties of foams for use as a synthetic growing media.

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Abstract

Common substrates used in soilless cultivation of vegetables have been shown to have several drawbacks including variability of organic substrates and disposal of some inorganic substrates.. Polyurethane foams (PUF) meet several of the requirements to be a synthetic growing medium.. However commercial formulations are not optimised for hydroponics and the addition of a functional filler could improve these properties. Sodium bentonite was added to foam formulations due to its use as a soil amendment which improves the water holding and cation exchange capacity (CEC) of soils. Sodium bentonite was added at loadings varying between 0 – 20 PPHP. The addition of bentonite increased PUF density from 41.1 kg.m^{-3} to 48 kg^{-3}, increased water holding content from 464 g.dm^{-3} to 767g.dm^{-3} , increased CEC from 0 to 4.65 cmol$_c$.kg^{-1} and increased the number of open cells visible in SEM images. The water drop penetration time decreased from 132 min to 78 min and the compression force deflection decreased from 10.6 kPa to 6.2 kPa. These physical and chemical changes improved tomato variety Sub arctic plenty vegetative growth, dry shoot mass increasing from 7.2 g to 12.9 g at a loading of 10 PPHP sodium bentonite.

Keywords: Polyurethane foam, synthetic media, bentonite, hydroponics

INTRODUCTION

The degradation of soils globally and uncertainty of weather patterns due to climate change are putting a major strain on conventional food production (FAO, 2015) and controlled environment agriculture (CEA) offers an alternative method for production of food, which is unaffected by the above problems. Synthetic growing media is often used in CEA, and consists of organic and inorganic substrates.

Organic substrates such as coco coir, tree bark, rice hulls/husks and sawdust offer an environmental advantage as they are often a waste product from another industry and locally available. However, these substrates' physical properties can change as the media degrades (Bilderback et al., 2005) and they are often not optimised for plant growth (Bunt, 1988). Furthermore, organic growing media are often non uniform, which can hamper yield for commercial growers who need to produce healthy uniform plants to precise time scales (Barrett et al., 2016). Peat also falls into this category, however significant exploitation of species-rich bogs has led to significant pressure to reduce its use for horticultural applications (Barkham, 1993).

Inorganic substrates make up the major share of soilless media due the consistency of the manufacturing process as well inert nature of the virgin product (Bussell and Mckennie, 2004). They are however not without problems. Life cycle analysis of a multi-tunnel greenhouse in Almeria, Spain showed that the growing media (perlite) was a major environmental burden, due to large amount of energy required for its production (Torrellas et al., 2012). Similarly, rockwool manufacturing has a large primary energy requirement and

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releases 167 kg of CO_2 into the environment per cubic meter produced (Dannehl et al., 2015). In both cases, waste disposal adds to the environmental footprint of the substrate as they are often disposed of after one growing season and in many cases it is sent to landfill in the absence of viable recycling pathways. An exception to this is the recycling of rockwool, which is successfully done by manufacturers in the Netherlands and UK ensuring little waste enters landfill (Bussell and Mckennie, 2004). These environmental issues have led to research being done into more sustainable alternatives.

Polyurethane foam (PUF) has long thought of to be a suitable synthetic soil, with the first patent for this use being issued in 1976. PUF substrates have been reused as synthetic growing media for up to 10 years (Benoit and Ceustermans, 1995) and can even improve over successive crops with roots improving the water holding capacity (Hardgrave, 1995), presumably as a function of sequential organic matter retention. This early work often used PUF from other industries, that were not optimised for horticultural use, therefore more recent work has developed foams with support from polyurethane manufacturers and have matched or exceeded rockwool as a synthetic media (Huber et al., 2005). Although there has been little work done on life cycle analysis of PUF for use as a synthetic growing media, EUROPUR has calculated the CO_2 cost of MDI based PUF as 2.95 kg CO_2 per kg of foam. This equates to 132 kg of CO_2 produced per cubic meter of foam at a density of 45 $kg.m^{-3}$ (EUROPUR, 2015).

While a major focus in the development of PUF for horticulture has been water retention, the largely inert surfaces of the foam results in both poor buffering capacity and nutrient retention. The inclusion of clay particles, which serve to enhance the water and nutrient retention in natural soils may represent a potential solution to both of these issues in horticultural PUF. For example, bentonite clays have a high water holding capacity and cation exchange capacity and this has in turn led to them being used as soil additives, where they can improve water retention of soils and act as stabilising aid to any liquid fertiliser (Murray, 2006). Moreover, sodium bentonite has been used as an additive in polyurethane foams as a cell opener (Harikrishnan et al., 2006) and at low loadings has improved mechanical strength and flame retardancy of PUF in a non-horticultural context (Rastin et al., 2016) but may secondarily enhance the properties of PUFs for horticultural use as synthetic substrates.

The aim of this research is to determine whether the addition of sodium bentonite to a standard flexible PUF formulation, improves tomato growth by changing the physical and chemical properties of the PUF.

MATERIALS AND METHODS

PUF components

The polyol used for all samples was Voranol 3322, a polyether triol, with a molecular weight of 3500 and a hydroxyl number of 48 supplied by DOW chemicals. The isocyanate used was Specflex NE 112, a low functionality polymeric methylene diphenyl diisocyanate based isocyanate, with an isocyanate equivalent of 130 and NCO content of 32 %. This was also kindly supplied by DOW chemicals. A silicone surfactant, Tegostab BF2470 was supplied by Evonik Industries. The two amine catalysts, Dabco 33LV and dimethylethonalamine (DMEA) were purchased from Sigma-Aldrich, to be used as a gelling and blowing catalyst respectfully. Sodium Bentonite was purchased from Alfa Aesar and distilled water was used as a blowing agent.

Synthesis of PU foams

A basic flexible polyurethane formulation was used for all samples (Table 1). All components were kept constant and only the amount of bentonite clay was varied with 0, 1.12, 2.75, 4.75 and 10.1 g of sodium bentonite added per 100g of PUF. This achieved concentrations of 0, 2, 5, 10 and 20 parts per hundred parts of polyol (PPHP) respectively in the resultant PUFs. However, at high loadings of the clay (10 PPHP and 20 PPHP) the blowing catalyst needed to be increased to a loading of 1 PPHP to produce stable foams.

Table 1. Flexible PU foam formulation

Component	Description	Part by weight
Polyol	Voranol 3322	100
Water	Distilled	4
Silicone Surfactant	Tegostab BF2470	0.65
Gelling Catalyst	Dabco 33LV	0.3
Blowing Catalyst	DMEA	0.5 *
Isocyanate	Specflex NE 112	70.1
Bentonite	Sodium Form	0 – 20

*DMEA needed to be increased to 1 PPHP for 10 and 20 PPHP loadings of Sodium Bentonite in order to achieve stable PUF.

All components except the isocyanate were weighed and then mixed using an overhead mixer with a three blade propeller type impeller at 3000 RPM for 90 seconds. The resultant mixture of components was degassed for 5 minutes, by leaving the sample to stand in the fume hood. The stoichiometric amount (R = 1) of isocyanate was added and this was mixed for 15 seconds at 3000 RPM. The reacting foam was transferred to a clean polypropylene cup or plant pot.

Physical Property characterisation

Density of the PUF formulations was measured according to ASTM D3574-11 test A. Compression force deflection (CFD) was measured according to ASTM D3574-11 test C, using a Zwick/Roell Z0.5. Water holding capacity (WHC) was measured by submerging a sample of dimensions of 50 × 50 × 25 mm^3 (L × W × H) and of known mass in deionised water for 24 hours. Samples were removed and left to drain for 15 minutes before being weighed. The WHC was measured by subtracting the dry mass from the wet mass and dividing by the samples volume. Air filled porosity was calculated by subtracting the water porosity (calculated from the WHC) from the total porosity (calculated from bulk density). A water drop penetration test (WDPT) was performed by placing a drop of 1 % bromophenol blue solution on the sample surface and measuring the amount of time taken for the droplet to be completely absorbed by the foam. This test is often done in soil sciences to determine the hydrophobicity of a soil (Doerr, 1998). This was repeated five times on each foam sample, and repeated on three different samples from each formulation. The time in minutes is reported. Scanning electron microscopy (SEM) was used to gain further insight into the morphology of the foam samples. Samples were gold coated (15mA, 2 minutes) and then imaged using an Inspect F SEM at an accelerating voltage of 10kV. Cell size was determined using optical microscopy. The cation exchange capacity of the foams was calculated by reacting the PUF with a 0.01 M $[Cu(trien)]^{2+}$ solution, and then measuring the change in concentration of copper using UV/Vis spectroscopy (Ammann et al., 2005). Absorption was measured at 577 nm on a Varian Cary 50 Probe UV vis spectrophotometer (Reganold and Harsh, 1985).

Characterisation of sodium bentonite

The CEC was determined using the same methods those for the PUF. The reacted $[Cu(trien)]^{2+}$ solution was further analysed on a Spectro-Ciros-Vision Optical Emission Spectrometer (ICP-OES) to confirm the CEC and determine the elemental composition of the ions leached from the sodium bentonite.

Growth Trials

This study was carried out in a temperature controlled greenhouse with a day/ night regime of 12 h at 20 °C / 12 h at 15 °C from 2018/03/09 until 2018/04/20 (6 weeks). Supplementary lighting was used to achieve a minimum solar irradiation of 1000 $W.m^{-2}$ (Phillips Mastercolour CDM-T Elite MW 315W/942 1CT). The only variable tested was sodium bentonite loading, which was varied between 0, 2 and 10 PPHP. Pots with a diameter of a 12 cm and a volume of 1 l were used. Seeds of *S. lycopersicum* var. Subarctic plenty (Premier Seeds Direct, Wiltshire, UK) were pre-germinated and one seedling planted per pot with 5 replicates at each clay loading. Growing conditions followed the guidelines set by Schwarz et al., 2014. Plants were supplied with Long Ashton solution (Hewitt, 1966) via a dripper feed delivering 2 $l.\ hr^{-1}$.

The solution was changed every two weeks and the concentration sequentially increased from 20 %, to 40 % and to 60 % strength over the 6 week growth period. pH of the nutrient solution was maintained between 5.5 and 6 and was adjusted using a 10% phosphoric acid solution.

Plant heights were measured twice a week during the trial, and at the end of the trial above ground biomass was harvested, dried for 5 days at 70 °C and weighed.

Statistical analysis

Differences in PUF physical properties were analysed by 1-way ANOVA, followed by Tukey multiple comparison test. Differences between treatment means of plant height were analysed by repeated measures analysis of variance (ANOVA) and differences between treatment means of above-ground biomass as well as integrated area under plant height curves were analysed by 1-way ANOVA, followed by Tukey multiple comparison test using the Minitab Statistical package (Version 18, Minitab LLC, State College, USA). All graphs plotting and curve fitting was done in R stats (R Core Team, 2013).

RESULTS AND DISCUSSION

Polyurethane foam properties

Density of the foam increased linearly with an increase in sodium bentonite clay loading, from 41.1 $kg.m^{-3}$ with no clay to 48 $kg.m^{-3}$ with 20 PPHP clay (Fig. 1A).

Compression force deflection (CFD) was reduced with the addition of any sodium bentonite clay (Fig. 1B), this reduced to a minimum at a loading of 10 PPHP of clay. Any further increase of clay had little further effect on the CFD.

Water holding content (WHC) increased drastically from 464 $g_{H2O}.dm^{-3}$ to approximately 700 $g_{H2O}.dm^{-3}$ with 2 PPHP of clay and only increased slightly higher with any further addition of clay (Fig. 1C). Water drop penetration time (WDPT) decreased to a minimum at 5 PPHP, and further addition increased the WDPT slightly (Fig. 1D). It needs to be noted that these foams would still be considered severely hydrophobic (Bisdom et al., 1993) and the WDPT would need to be decreased to less than 5 seconds to be considered a hydrophilic growing media.

CEC of the foams increased linearly with an addition of sodium bentonite (Fig. 1E). The CEC was lower than calculated CEC, indicating that some of the sodium bentonite was trapped within the polyurethane matrix and water was unable to penetrate these clay particles and exchange cations.

The air filled porosity of the foams decreased from 0.5 $m.m^{-3}$ to 0.28 $m.m^{-3}$ at 2 PPHP sodium bentonite. The air filled porosity decreased slightly with further addition of bentonite however this was not significant (Fig 1F).

The number of open cells of the foams increased with the increased sodium bentonite loadings. This is visible in Fig. 2. Even at the highest loading there is still a large proportion of closed cells, this may be one of the reasons for high WDPT times. The sodium bentonite loading and no effect on cell size of the PUF, diameters of cells were between 380 – 400 µm for all samples.

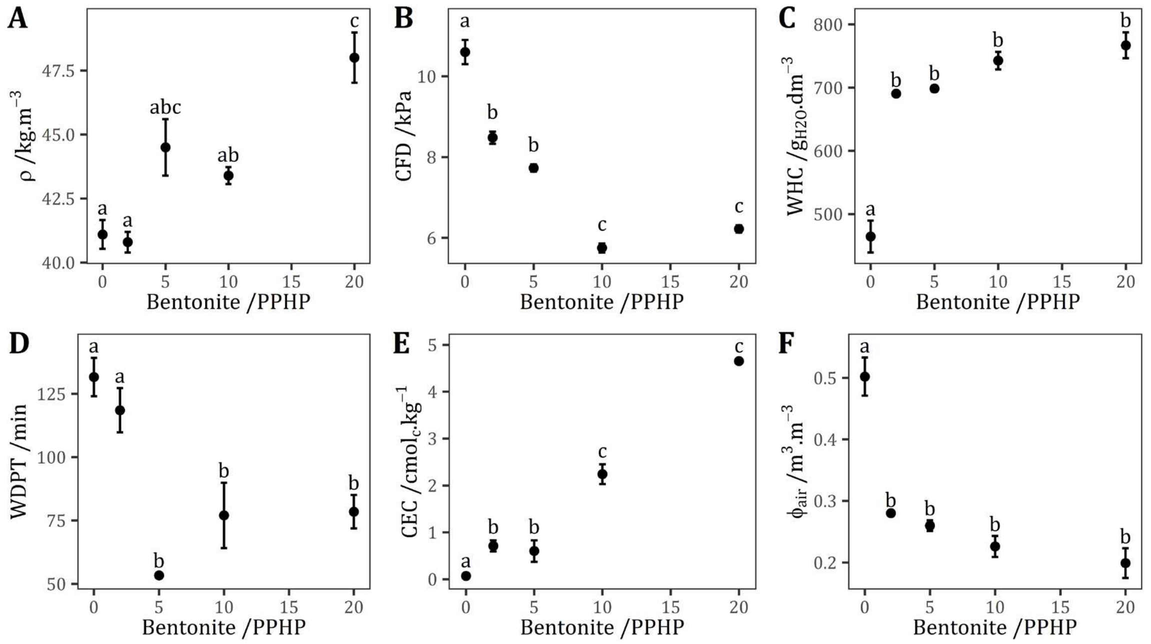

Figure 1. Physical properties of PUF with varied sodium bentonite loading. (A) density, (B) compression force deflection, (C) water holding capacity, (D) water drop penetration time, (E) cation exchange capacity, (F) air filled porosity. Error bars represent ± 1 standard error. Points with differing letter codes are significantly different (ANOVA followed by Tukey multiple comparison test at $P<0.05$, see table 2).

Table 2. Results from the analysis of variance for polyurethane foam physical properties

Property	d.f.	F	*P*
Density	4,10	9.63	0.002
CFD	4,10	90.66	<0.001
Log_{10}(WHC)*	4,9	28.87	<0.001
WDPT	4,10	11.04	<0.001
CEC	4,10	9.63	<0.001
Air Filled Porosity	4,9	34.68	<0.001

* Data were Log10 transformed due to lack of homogeneity of variance and analysed by ANOVA, untransformed data are presented in Figure 1.

Sodium bentonite characterisation

Sodium bentonite cation exchange capacity (CEC) was calculated to be 93.6 ± 0.77 cmolc.kg^{-1} via UV vis, this corresponded closely to ICP results, where CEC was calculated as 97.23 cmol$_c$.kg^{-1}. Table 3 shows some of the ions and their concentration (mg.l^{-1}) that were exchanged out of the clay, several of these are important micronutrients that promote plant growth.

Table 3. Concentrations of some elements exchanged out of sodium bentonite

	B	Ca	K	Mg	Na	S	Si	Zn
Concentration (mg.l^{-1})	0.057	47.2	8.08	17.2	278	48.5	1.12	0.04

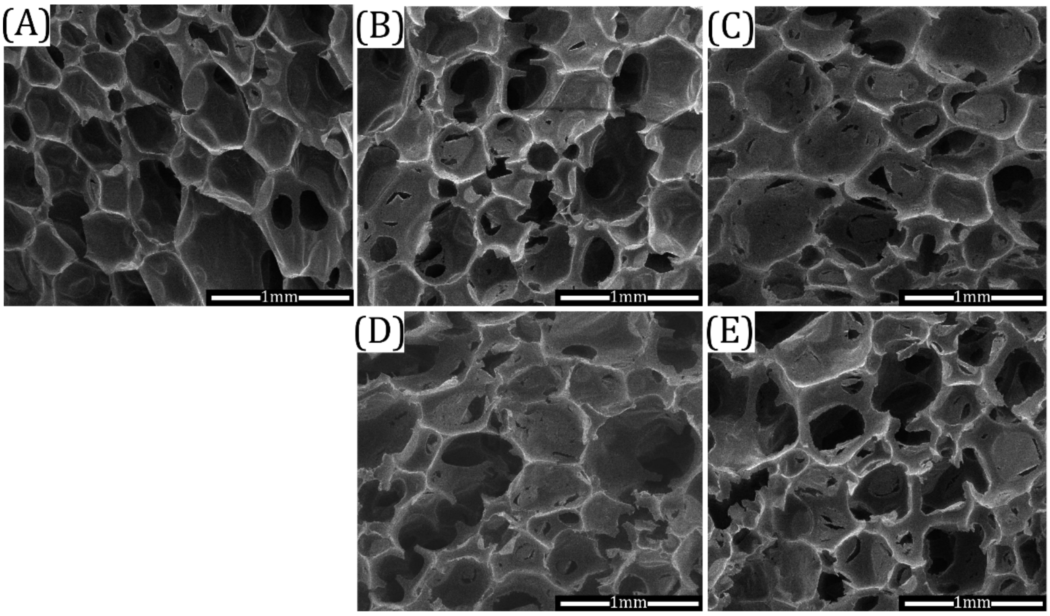

Figure 2. Scanning electron microscopy images of PUF with increasing amounts of sodium bentonite (A) 0 PPHP, (B) 2 PPHP, (C) 5 PPHP, (D) 10 PPHP, (E) 20 PPHP.

Growth Trials

Figure 3 shows the plant heights grown in PUF with varying clay loadings as a function of time. As anticipated, the height of the tomato plants increased over time (ANOVA: d.f. = 15, 170; F = 1912.9; $P < 0.001$), the plant height was also increased by the addition of sodium bentonite (ANOVA: d.f. 2, 170; F = 151.04; $P < 0.001$). This effect was confirmed by integrating the area under each of the plant height fitted curves. Figure 4A shows the increase of the area under curve (AUC) with increase in clay loading. The PUF with no clay and 2 PPHP were not significantly different, and only at 10 PPHP clay was there a significant increase in plant growth.

Plant shoot mass increased with an increase in sodium bentonite loading. Figure 4B shows dry shoot mass of tomato plants grown in PUF. The Tukey multiple comparison test again showed that there was only a significant increase in dry mass between the foam with no clay and the PUF with the highest loading of clay.

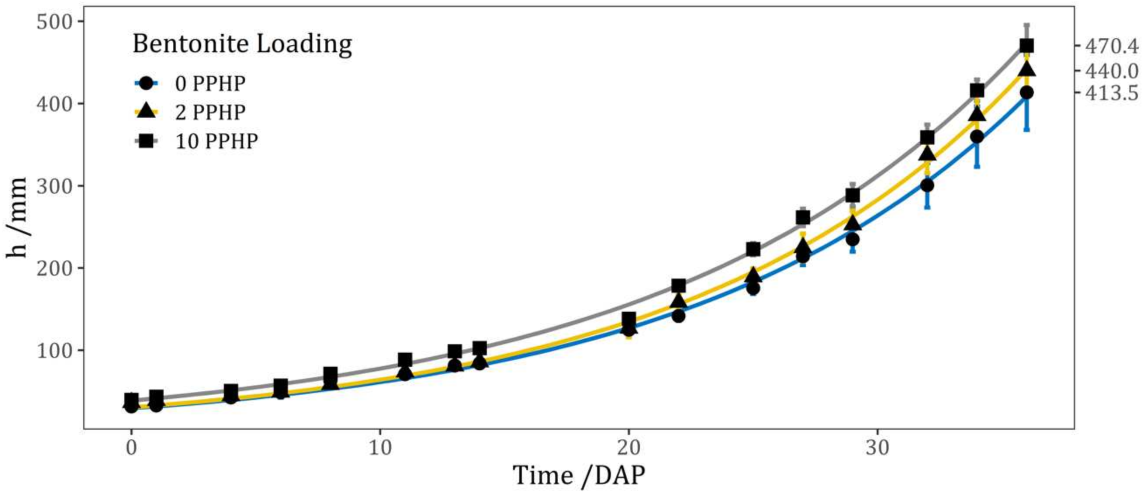

Figure 3. Height of plants grown in PUF with varying amounts of sodium bentonite, final plant heights (mean) shown on right. Error bars represent ±1 standard error.

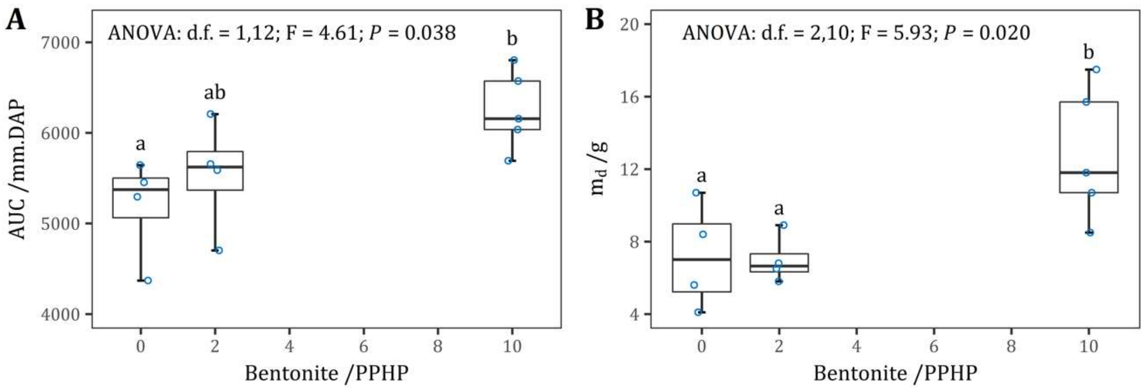

Figure 4. (A) The indicated area under curve (AUC) of plant heights with varied sodium bentonite loadings. (B) The dry mass of shoots with varied sodium bentonite loadings. Points with differing letter codes are significantly different (ANOVA followed by Tukey multiple comparison test at $P<0.05$). Box plots show median, 1st and 3rd quartile and whiskers show maximum and minimum points.

Analysis of any individual physical or chemical properties showed that no single property had significant influence on the AUC or shoot dry mass of plants. This indicates that the improved growth is a function of several of the changes caused by the addition of sodium bentonite. The majority of physical (all except density) and chemical properties were significantly different at 10 PPHP loading when compared to the sample with no sodium bentonite, and the combination of these properties improved vegetative growth of tomato plants.

CONCLUSIONS

Tomato plants were successfully grown hydroponically in a novel polyurethane foam substrate with varying levels of sodium bentonite addition. The addition of the clay had several impacts on the physical and chemical properties of the foam. The clay increased density, water holding, water penetration as well the degree of open cells in the foam. Whilst the mechanical properties of the foam deteriorated with increased clay loading, improved water holding and cation exchange capacity was introduced into the foams, allowing nutrients to be stored in the substrate. The combined changes to physical and chemical properties of the foam improved tomato growth in the hydroponic system, with both the wet and the dry mass of the shoots increasing significantly with an increase in sodium bentonite loading. The PUF media would still be classed as a highly hydrophobic, due to the high water penetration time and developments in foam formulations to reduce this may further improve plant growth.

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