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Experimental design as a framework for optimising polyurethane foam as a soilless growing media.

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Abstract

The increasing use of soilless cultivation for the production of fruit and vegetable crops allows for constant innovation and development of new soilless growing media. Flexible polyurethane foams (fPUF) have many of the properties required for this purpose. They have the mechanical strength to anchor plants and their highly porous nature allows for liquid and gas transfer to occur in the polymer foam cells. However, the optimum PUF physical properties required for efficient plant growth have not been well explored. Design of Experiment (DoE) techniques were used to generate 15 fPUF's with a large range of select properties by varying catalyst and surfactant ratios. Density, cell size, water holding capacity (WHC), water drop penetration time (WDPT) and airflow were selected as foam properties likely to influence plant growth. Airflow ranged between 0.970 - 108 $\mathrm{l.min^{-1}}$, foam cell size ranged between 0.966 – 1.98 mm, density of foams ranged between 30.4 – 41.9 $\mathrm{kg.m^{-3}}$, WDPT ranged between 0.500 – 6050 s and WHC ranged between 204 – 966 $\mathrm{g_{H2O}.l_{foam}^{-1}}$. Spring onions (*Allium cepa*) were grown hydroponically in the fPUF and plant height, dry shoot mass, nitrogen content and phosphorus content were measured. These response variables were modelled using the foam physical properties as factors. Water holding as well as the foam cell size were the only significant factors in determining the plant height, nitrogen content and phosphorus content. Water holding, cell size as well as airflow through the foam were significant factors in predicting the dry plant mass. All responses were successfully modelled using a DoE framework, indicating the strength of such a methodology in optimising fPUF as a soilless growing media.

Keywords: Polyurethane foam, synthetic media, experimental design, hydroponics

INTRODUCTION

The global food supply chain is under strain due to increasing population as well as climate change (FAO, 2015), while simultaneously representing a major source of greenhouse gasses, with 24% of all global greenhouse gas (GHG) emissions generated by agriculture (FAO, 2006) and consuming 85% of the World's fresh water (Falkenmark and Rockstrom, 2004). The use of inorganic nitrogen fertilizer represents one of the key sources of these emissions, with over 40% of the embedded GHGs attributable to this source in some supply chains (Goucher et al., 2017). Controlled environment agriculture (CEA) offers an alternative method for production of food that offers dramatically lower water and inorganic nutrient requirements. The increased use of CEA and hydroponic techniques, expected to grow by 9.2% in value in the USA between 2020-2025 (Engler and Krarti, 2021) means that there is a gap in the growing media market for novel media. This is predicted to be 65 $\mathrm{Mm^3 year^{-1}}$ by 2050 (Chris Blok, 2020).

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Flexible polyurethane foams (fPUF) can be tuned such that the properties are suitable as soilless growing media, by optimising the reaction chemistry. Research into fPUF as a substrate has indicated that PUF substrates can be reused for several growing seasons (Benoit and Ceustermans, 1995) and growth can even improve over successive crops (Hardgrave, 1995). 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). Recycled polyurethane mattresses have even been used in refugee camps in Jordan as a physical support for low tech hydroponically grown crops (Al Meselmani et al., 2020). Previous work by the authors used sodium bentonite as a functional filler in fPUF media, which improved plant growth. However, the addition of this filler also changed the foams physical properties meaning it was not possible to determine which physical properties were impacting plant growth (Wright et al., 2021).

The aim of this work is to determine whether plant growth responses can be modelled from fPUF physical properties using a design of experiments (DoE) approach. This would be achieved by generating a large number of foam formulations with a wide range of physical properties, characterising the foam and then growing a quick yielding and compact crop (spring onion) and finally measuring and modelling important plant growth responses.

MATERIALS AND METHODS

PUF components

The polyols used for foam preparation were Voranol 3322, a polyether triol, with a molecular weight of 3500, Voranol 1447, a high ethylene oxide content polyether triol with a molecular weight 4610 and Specflex Activ 2306 a catalytically active polyether polyol. The isocyanate used was Specflex NE 112, a low functionality polymeric methylene diphenyl diisocyanate based isocyanate with an NCO content of 32 %. Polyols and isocyanates were kindly supplied by DOW Chemical Company (Michigan, United States). Two silicone surfactants, Tegostab BF2470 and Tegostab 8476 were supplied by Evonik Industries as was the amine based blowing catalyst, dimethylethonalamine (DMEA). Sodium Bentonite was purchased from Alfa Aesar and distilled water was used as a blowing agent. All reagents were used as received.

Synthesis of PU foams

The formulation used for the fPUF's is shown in Table 1. Only the two catalysts (Specflex Activ 2306 and DMEA) and surfactants (Tegostab BF2470 and Tegostab 8476) were varied between samples, as it was expected that changing the quantities and ratios of these components would give foams with widely ranging physical properties. The polyol, Voranol 3322 was varied with the amount of SpecFlex Activ 2306 to ensure that the sum of the parts of all polyols was 100. All components except the isocyanate were weighed and then mixed using an overhead mixer with a turbine stirrer at 3000 RPM for 45 seconds. The resultant mixture of components was allowed to debubble for 5 minutes. The required amount of isocyanate was added and this was mixed for 5 seconds at 3000 RPM. The reacting foam was transferred to a clean polypropylene cup or plant pot.

Table 1. Flexible PU foam formulation

Component	Description	Part by weight
Polyol	Voranol 3322	15-25
Polyol	Voranol 1447	75
Catalytic Polyol	SpecFlex Activ 2306	0-10
Water	Distilled	4
Silicone Surfactant	Tegostab BF2470	0-1
Silicone Surfactant	Tegostab 8476	0-1
Blowing Catalyst	DMEA	0-2
Isocyanate	Specflex NE 112	73
Bentonite	Sodium Form	30

Physical Property characterisation

Five fPUF physical properties likely to influence plant growth were selected and methods that allowed for rapid measurements of these properties were developed. Airflow was determined using an airflow meter designed according to ASTM D3574-11 test G, the airflow is measured through the foam at a constant vacuum pressure of 125 Pa. Airflow is reported in $l.min^{-1}$ and was identified as an important foam physical property as it can be used as an indirect measure of the ratio of open to closed cells in a fPUF (Yasunaga et al., 1996). Cell size was determined using optical microscopy according to ASTM D2576-15 and is reported in mm. Density of the foams was measured according to ASTM D3574-11 test A. A water drop penetration test (WDPT) was performed by placing a drop of 1 % bromophenol blue solution (to increase optical contrast) on the sample surface and measuring the amount of time taken for the droplet to be completely absorbed by the foam. fPUF hydrophobicity could then be ranked according to Doerr, 1998. This was repeated five times on each foam sample and the WDPT is reported in seconds. Water holding capacity (WHC) was measured by submerging a sample of dimensions of 50 × 50 × 25 mm^3 in deionised water for 24 hours. Samples were removed from the water and left to drain freely for 15 minutes before being weighed. The difference between the foams wet and dry mass was used to determine the WHC, by dividing this value by the volume and WHC is reported in $g_{H2O}.l_{foam}^{-1}$.

Growth Trials

This plant growth study was carried out in a temperature controlled greenhouse at the Arthur Willis Environmental Centre (AWEC) at the University of Sheffield with a day/ night regime of 12 h at 20 °C / 12 h at 15 °C from 2019/05/15 until 2019/07/16. Supplementary lighting was used to achieve a minimum solar irradiation of 1000 $W.m^{-2}$ (Phillips Mastercolour CDM-T Elite MW 315W/942 1CT). Pots with a diameter of 15 cm and a volume of 1400 ml were used. Spring onion (*Allium cepa)* seeds of the variety White Lisbon (Premier Seeds Direct, Wiltshire, UK) were pre-germinated and transplanted to Grodan rockwool starter cubes on 2019/04/23. These seedlings were transplanted into foam on 2019/05/15. Five seedlings were planted per pot with five replicates for each formulation for a total of 350 plants. Plants were supplied with Long Ashton solution (Hewitt, 1966) via a dripper feed delivering 2 l. hr^{-1}. The drippers were on a timer supplying the plants with nutrient solution for 15 minutes each day. The solution was changed every two weeks and the concentration sequentially increased from 20 %, to 40 % and to 60 % (Long Ashton solution) strength over the 8 week growth period. The pH of the nutrient solution was maintained between 6 and 6.5 and was adjusted using a 10 % phosphoric acid solution.

Plant growth analysis

Plant height was measured twice a week as well as at the end of the experiment and is reported in mm. Dry shoot mass was determined by drying the plant shoots to constant mass at 70 °C and weighing the sample and is reported in g.plant^{-1}. Dried shoots were homogenised and acid digested with concentrated sulphuric acid at 350 °C for 15 minutes with a hydrogen peroxide addition for N and P determination (Murphy and Riley, 1962). N and P content was determined spectrophotometrically from a dilute sample of the acid digested shoot (John, 1970; Krom, 1980) and both N and P are reported in mg.g$_{dryshoot}^{-1}$.

Statistical analysis

Differences in plant growth responses were analysed by 1-way ANOVA using R stats. Modelling of plant growth responses as functions of fPUF physical properties was done using k-fold cross validation (k = 3) and elastic net regression, using JMP®, Version 14.3 SAS Institute Inc., Cary, NC, 1989-2019. All graphs plotting and curve fitting was done in R stats (R Core Team, 2013).

RESULTS AND DISCUSSION

Polyurethane foam properties

Figure 1 shows the experimental space covered by the fifteen fPUFs (referred to as GK01 to GK15) generated by varying the surfactant and catalyst loadings. Physical properties are rescaled between -1 and 1 to help view the entire experimental space on a single figure. Sample GK07 is excluded from all analysis as this sample collapsed during reaction, indicating an unstable foam formulation. Airflow through the samples ranged from 0.970 - 108 l.min^{-1}, indicating that foam cell windows ranged from fully closed to fully open and this result was confirmed by scanning electron microscopy. Cell size ranged from 0.966 – 1.98 mm, with one formulation (GK05) having drastically larger cell size than the rest. The optical micrograph from GK05 is shown in Figure 2 (A), this is contrasted with the micrograph from a formulation with a more representative cell size in Figure 2 (B). Density of foams ranged from 30.4 – 41.9 kg.m^{-3}. Water drop penetration time (WDPT) ranged from 0.500 – 6050 s, indicating a broad range of foams ranging from “very hydrophilic” to “very strongly hydrophobic” (Doerr, 1998). Water holding capacity (WHC) ranged from 204 – 966 g$_{H20}$.l$_{foam}^{-1}$, giving a broad range of WHC values. Figure 1 shows these unscaled ranges on the right, and also follow a property trace of two different formulations, GK05, in red and GK14 in green.

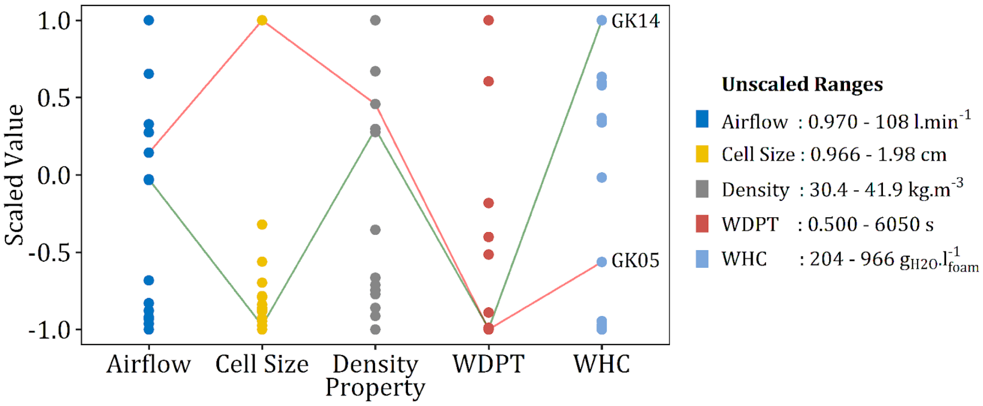

Figure 1. Experimental space of various physical properties of the 15 different fPUF substrates, rescaled between -1 and 1, with the unscaled ranges shown on the right. A property trace for formulation GK05 is shown in red and a property trace for GK14 is shown in green.

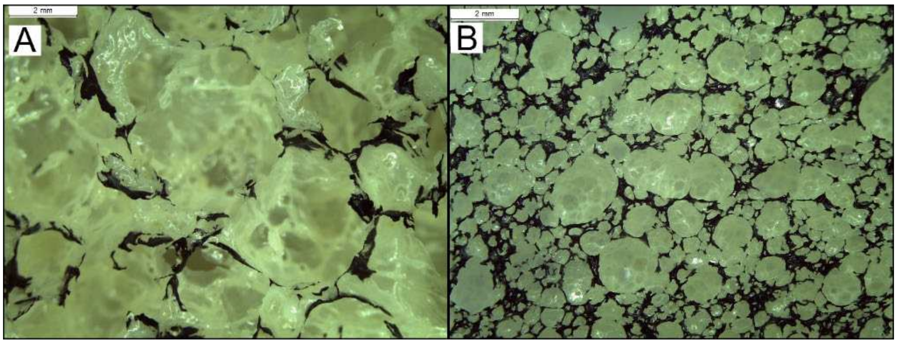

Figure 2. Optical microscope images of (A) fPUF (GK05) with a vastly different cell size to the other formulations and (B) a fPUF with more regular cell size.

Growth Trials

Survivability of plants was monitored throughout the experiments and is plotted in Figure 3 (A) as a Kaplan-Meier survivability plot. Two fPUF formulations, GK05 and GK06 differed significantly from a zero deaths plot using a log rank test. Figure 3 (B) shows the plant heights for the different formulations over time. These heights are fitted with an exponential curve and the area under the curve (AUC) is determined by integrating beneath the area for each sample. Figure 4 shows the mean values and standard error for the four response variables (A) AUC, (B) dry shoot mass, (C) Nitrogen content and (D) Phosphorus content with the results from a one way ANOVA, with each formulation as a factor is also shown. The ANOVA analysis indicated that the fPUF formulation significantly affected each of the four plant growth responses.

By following the property traces of specific formulations, we can gain further insight into which properties are affecting plant growth response. The red trace in Figure 1, shows the properties for the worst performing foam in terms of dry shoot mass, GK05, and the green trace shows the properties of the best performing foam in terms of dry shoot mass, GK14. Both foams have similar densities, airflow and WDPT however their WHC and cell sizes vary significantly. GK05 has the largest cell size and low WHC whilst GK14 has much lower cell size and the highest WHC. This is the first insight that these foam properties are important for predicting plant growth.

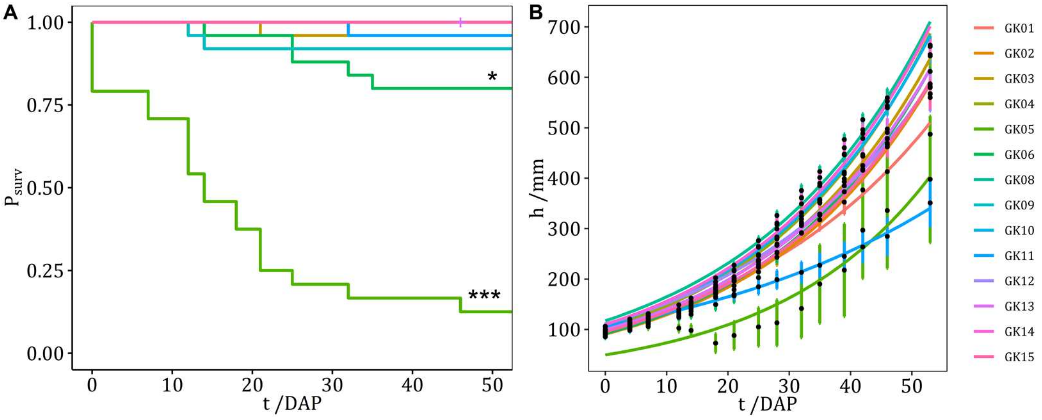

Figure 3. (A) The Kaplan-Meier survivability plot for the different foam formulations. Asterisks indicate significant differences from zero deaths, $*p < .05$, $***p < .001$ (log rank test). GK05 and GK06 are the only formulations significantly different from zero deaths. (B) Plant height curves for the different fPUF formulations with fitted exponential curves used to calculate the AUC.

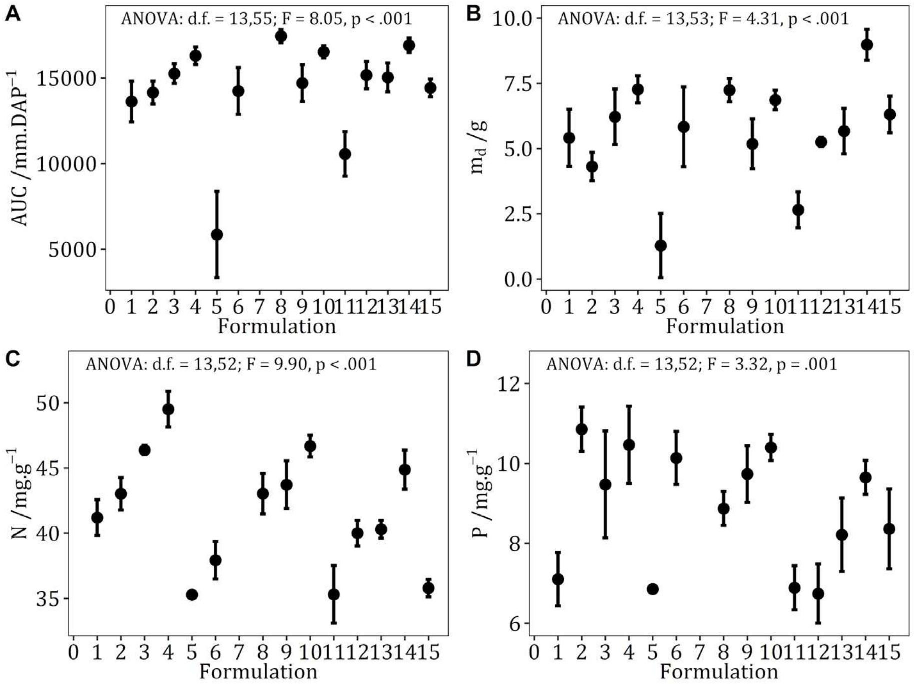

Figure 4. (A) AUC values, (B) dry shoot mass. (C) shoot Nitrogen content and (D) shoot Phosphorus content for the spring onion grown in different foam formulations with the results for a one way ANOVA given for each response. The error bars represent ±1 standard error.

To further explore possible relationships between plant growth responses and foam physical properties a DoE modelling approach was taken. Models of the general form shown in Equation 1 were fitted to each of the responses.

$$z_i = \sum_{1 \le i \le q} \beta_i \alpha_i + \sum_{1 \le i \le q} \beta_{ii} \alpha_i^2 + \epsilon \qquad 1$$

Where z_i is the response variable, β are fitting parameters, α_i are the fPUF physical properties (α_1 airflow, α_2 cell size, α_3 density, α_4 WHC, α_5 WDPT) and ϵ is the model error (a term that accounts for variation due to other factors). This type of general model accounts for linear relationships as well any curvature. General models were then reduced using k-fold cross validation and elastic net regression, leaving only the statistically significant terms. An example of this for the AUC response variable follows.

Response Modelling (AUC example)

The AUC model reduces to a simple linear model, with α_2 (cell size) and α_4 (WHC) as the only significant factors. The reduced fitted model is shown in Equation 2.

$$AUC = - 1.65\alpha_2 + 0.000502\alpha_4 + 2.02 \qquad 2$$

Plotting the observed AUC as a function of the predicted AUC yields Figure 5 (A), which has an $r^2 = 0.91$, showing a good fit between the observed and predicted values. The fit line also follows the y = x line (black dashed line) closely. By looking at the t-ratio for each of the terms, we gain further indication of their statistical significance. The greater the value of the t-ratio test the greater the significance of the term. The sign of the t-ratio tells us whether the term is positive or negative, and a t-ratio term with an absolute value of more than two indicates that the term has a p-value < .05. Figure 5 (B) shows the t-ratio for the terms in the AUC model and we can see that cell size has the most influence on the AUC and a negative value, indicating that larger cells reduce growth. The error constant and the WHC are both also significant and both are positive, this indicates that an increase in WHC increases plant growth. As there are only two factors that are significant we can view the AUC as a function of the two factors on a contour plot. The near vertical lines in the contour plot in Figure 5 (C) again indicate the important role of cell size in predicting AUC.

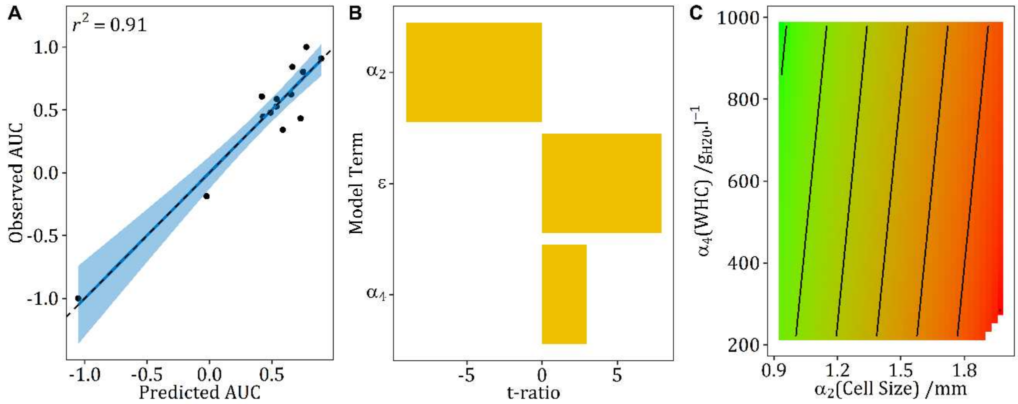

Figure 5. (A) The observed AUC as a function of the predicted AUC for the selected optimum model, the confidence interval shown in blue, with the y = x line shown as a dashed black line. (B) the t-ratio terms for the AUC model terms where α_2 is the cell size and α_4 is the WHC and (C) a contour plot showing the influence of cell size and WHC on the AUC with red indicating low AUC and green indicating high AUC.

This methodology was followed for modelling all the plant responses, and Table 2 gives a summary of these models. The cell size and WHC was significant for all the responses and simple linear models such as the one shown in Equation 2 best fitted the AUC, N content and P content. The dry mass required a more complex model with airflow also being significant and with curvature in the airflow and the cell size terms. The fits for the N content and the P content were much lower though, with an r^2 = 0.69 for N and r^2 = 0.67 for P and although increasing the number of terms further increased the r^2 value, the kfold r^2 decreased, indicating that increasing the number terms decreased the robustness of the models.

Table 2: ANOVA results for the plant response models.

Property	**complexity**	**r^2**	**Kfold r^2**	**d.f.**	**F**	***p* value**
AUC	3	0.91	0.80	2,11	56.1	<.0001
m_d	6	0.96	0.76	5, 8	35.2	<.0001
N	3	0.69	0.37	2, 11	12.4	.0015
P	3	0.67	0.41	2, 11	11.2	.0022

CONCLUSIONS

A set of 15 fPUF were formulated with a large range of select physical properties. Airflow ranged between 0.970 - 108 $l.min^{-1}$, cell size ranged between 0.966 – 1.98 mm, density of foams ranged between 30.4 – 41.9 $kg.m^{-3}$, WDPT ranged between 0.500 – 6050 s and WHC ranged between 204 – 966 $g_{H2O}.l_{foam}^{-1}$. Spring onions (*Allium cepa*) were grown in a circulating hydroponic setup and plant growth responses, height, dry mass, N content and P content were measured. Plant growth responses were modelled using DoE techniques and the foam cell size and WHC were significant factors for all responses. The shoot dry mass required a more complex model where airflow through the foam was also significant as well as second order curvature terms for cell size and airflow. All models were statistically significant and explained a large portion of the variance indicating that a DoE approach is an appropriate and powerful technique for optimising a fPUF for predicting plant growth in hydroponic systems.

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