The Effect of Void Size and Level of Interconnectivity of Poly (S/DVB) HIPEs on Water Adsorption and Holding Capacities

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Abstract: **The global temperature has risen continuously over the past century, causing climate change all over the world and resulting in more and more extreme weather conditions. Many places have seen changes in rainfall, resulting in more floods, droughts, or intense rain, as well as more frequent and severe heat waves. The later oppose a severe thread to society by worsening the effect of urban heat island as well as leading to droughts, jeopardizing food production and security. Several measures to counteract the challenges imposed by climate change have be introduced. Most of which involving the planting of horticultural and even food crops in cities, e.g. vertically or on rooftops, in order to ease urban heat, by evaporation. Thus increasing the demand for water retentive, lightweight, and permanent material as soil additive and construction material. Poly HIPEs, porous emulsion-templated polymers, synthesized within high internal phase emulsions, have been used successfully used to reduce the water stress on crops, by incorporating them into the soil as an internal water storage medium. This study examines the relationship between void size and level of interconnectivity of Poly(S/DVB)HIPEs on water adsorption and holding capacities, and it suggests that there is a direct relationship between void size and water adsorption and holding capacities.**

Keywords: **high internal phase emulsion polymerization, PolyHIPEs, water adsorption capacity, water holding capacity, void size, agricultural applications.**

I. INTRODUCTION

Earth's average temperature has risen continuously over the past century, and it is projected to rise further over the next hundred years. Small changes in the average temperature of the planet can translate to large and potentially dangerous shifts in weather and climate. The evidence is clear; rising global temperatures accompanied by more and more extreme weather conditions. Many places have seen changes in rainfall, resulting in more floods, droughts, or intense rain, as well as more frequent and severe heat waves. The later oppose a severe thread to society by worsening the effect of urban heat island as well as leading to droughts, jeopardizing food production and security. In 2011, the economic loss due to drought in the southern United States alone accounted for more than US $ 10 billion [1]. Several measures to counteract the challenges imposed by climate change have be introduced. Most of which involving the planting of horticultural and even food crops in cities, e.g. vertically or on rooftops, in order to ease urban heat [2], thus increasing the demand for water retentive, lightweight, and permanent material as soil additive and construction material in order to cool down the immediate surrounding according to the evaporation heat [3,4]. Burke et. al. successfully demonstrated that polyHIPEs can be used to reduce the water stress on crops by incorporating them into the soil as an internal water storage medium. Their study revealed an increasing and faster rate of water uptake with increasing pore size and an increase of dry yield of up to 300% [4].

PolyHIPEs are porous emulsion-templated polymers, synthesized within high internal phase emulsions (HIPEs). Now known for many years [5], the generic term PolyHIPE was coined by Unilever researchers to describe these polymeric

foams [6]. Originally, PolyHIPEs were developed as carriers and absorbents for liquids [7,8]. High internal phase emulsions are highly viscous, paste-like emulsions [4], which make up a very concentrated dispersed systems [9] in which the dispersed phase occupies more than 74.05% of the whole volume fraction [1]. The major, dispersed phase is usually referred to as internal phase, the minor, continuous phase as external phase [4, 10, 11, 12, 13]. Throughout polymerization, holes develop in the external monomer envelope surrounding the discrete droplets owing to changes in surface tension and density [14].

The characteristic PolyHIPE monoliths are the result of the polymerization of the external phase around the droplets of the internal phase, followed by solidification of the external phase, the emulsion droplets are embedded in the resulting material [15]. Due to high concentration of the internal phase, droplet size distribution is usually polydisperse, and deformation into non-spherical shapes occurs, leaving only a thin film of external phase between adjacent droplets [9]. Subsequent removal of the internal phase gives rise to a porous replica of the emulsion [16].

The resulting porous matrix is characterized by a trabecular morphology [17] consisting of micrometer sized, almost spherical voids, interconnected via a plurality of much smaller pores, here referred to as windows [18], and the much smaller pores present within the walls of certain PolyHIPEs are referred to as pores [10]. Today there is a wide range of potential applications [15, 19, 20, 21, 22], ranging from oil recovery [23], over cosmetics to food preparation [24] as well as agricultural and horticultural applications [25]. In the later, a great potential is the use of PolyHIPEs is as a soil additive. Either as a water absorbing, lightweight construction material for urban agricultural practices and as a tool for climate change mitigation, or in agricultural production systems especially in semi-arid regions [25], where most soils have low water holding capacities.

There, it is of uppermost importance that a soil additive can quickly absorb large quantities of water, and can hold on to it for an extended period of time, but also release it as needed by the crops, and water absorption and retention are also important factors for the cooling effect by water evaporation.

In the literature, many papers [26, 27, 28, 29, 30] deal with the water uptake of different classes of porous materials, including paper, powders, rocks and soils, and a time dependent law of fluid absorption [31].

Bigger voids can absorb much more water at a much faster rate [4], making water absorption and retention dependent on the pore structures. However, these properties deteriorated with increasing pore size, or too high porosity, suggesting the small contact area of each pore to be effective to improve water retention at high porosity [32].

Since surface area and void size are strongly affected by the concentration of crosslinking co-monomer [33, 34] type and amount of surfactant [35] and type of inert diluent solvent [21, 33, 36, 37] it can be modified by a change in type and concentration of one or more of these factors. Especially the void size is strongly affected by the physiochemistry of the oil phase [35]. The phase percentage dictates the amount of oil that will surround a water droplet. Of course, the higher the percentage of the aqueous phase, the bigger and more interconnected the voids. However, if the emulsion viscosity is very high, the shear stress might not be sufficient to break up larger droplets, leading to a less interconnected structure [38]. The lowering of the cloud point by stabilizing salts effects increases the void size by controlling the packing density of surfactant molecules in the interfacial film [38]. The salt level of the emulsion was found to have a tremendous effect on the pore size. Thus a 10-fold reduction in cell size can be obtained by changing the conditions from no salt to 10 g of K_2S0_4/100 mL water, where most of the change occurs when the salt level has reached 0.005 g/100 mL [39]. The addition of a porogenic solvent dilutes the interfacial layers and leads to an increased void diameter [17].

To our best knowledge, nobody has investigated the relationship between void size and water holding capacity of PolyHIPEs. In order to better understand the mechanisms of water adsorption and holding capacity of these monoliths we investigated the relationship between void size and water holding capacity, aiming to identify the optimum void size for the previously mentioned specially applications.

II. EXPERIMENTAL

1. Materials

Styrene (S, Fluka), and divinylbenzene (DVB, Merck) was used as monomer and co-monomer to produce PolyHIPEs. The initiator and stabilizer used in the experiments were potassium persulfate ($K_2S_2O_8$, purity 98% (RT), Fluka Chemie) and calcium chloride (CaCl2, purity 97% (KT), Fluka Chemie) respectively. The surfactant sorbitan

monooleate (Span 80), and porogenic solvent tetrahydrofuran (THF) were purchased from Sigma-Aldrich Chemical. Sodium chloride was purchased from a local provider. All chemicals were used as received.

2. PolyHIPE preparation

A typical polyHIPE preparation [40, 41] was carried out, with the aqueous phase consisting of deionized water, a porogenic solvent (THF), salt, and an polymerization initiator ($K_2S_2O_8$). It was slowly and drop wise dosed into the oil phase of the emulsion, containing the monomer (S), the crosslinking agent (DVB), and the non-ionic surfactant (Span 80). Mixing was achieved by an overhead stirrer (IKA® RW 20 digital), equipped with a dissolver stirrer (IKA® R1303) set at 300 rpm, until all the aqueous phase had been added. The dosing time was 32 minutes, followed by 3 minutes homogenizing time, after which the emulsion was transferred into glass containers for polymerization, which were placed into a preheated water bath (memmert) of 60°C for 48h. the material was then removed from the glass containers to allow complete drying, in a convection oven at 60°C until constant weight was obtained. Due to the influential factors mentioned in the previous section, various systems, were used in order to get a wide range of different pore sizes and distributions. Firstly, the degree of the crosslinking agent (DVB) was varied (D in the code and the number indicate the ratio of DVB to S). Further, two different stabilizers were studied in this work: $CaCl_2$, and NaCl, both were held constant with respect to the total phase composition (C at the end of the code denotes a system based on $CaCl_2$, whereas N at the end of the code denotes a system based on NaCl), and the phase ratio of oil to aqueous phase was varied (the two digit figure after the letter A indicate the phase percentage of the aqueous phase), during these two experiments, the ratio of S to DVB was kept at a constant rate of 80:20. The initiator concentration ($K_2S_2O_8$) and the concentration of the porogenic solvent (THF) were held constant with respect to the total phase composition throughout all studied systems.

3. Characterization

Morphological characteristics, average pore size, and level of interconnectivity of each sample were examined by SEM (Hitachi S-4800), with an accelerating voltage of 10 kV. The specimens were coated with platinum under vacuum before testing to induce electric conductivity. The surface area was calculated from BET obtained from the N_2 adsorption-desorption isotherms at -196°C (Quantachrome Autosorb-iQ). Prior to analysis, the samples were degassed at 60°C for 12 hours in a vacuum furnace.

4. Water adsorption capacity experiment

The effect of the different void sizes on the water adsorption capacity of the obtained polyHIPEs was studied according to the principle described by Burke et. al. [25] . The samples were carefully cut with a scalpel into disks (2.5 x 0.5cm) and dried to constant weight (W_d) in a oven. Then the disks were fully immersed into deionized water, at room temperature, over several periods of time, given in table 1. After the removal from the water bath, they were dapped dry on the surfaces and their weight gain (W_s) was recorded. This experiment was carried out until equilibrium in weight gain was obtained.

The water adsorption capacity was calculated from the sample's weight gain, using formula 1:

$$\text{Water adsorption capacity} = (W_s - W_d)/W_d \qquad\qquad (1)$$

Where W_s and W_d are the weights of the soaked and dry samples, respectively.

5. Water holding capacity experiment

To determine the water holding capacity of the obtained polyHIPEs, samples were soaked until equilibrium was obtained. The fully soaked samples were removed from the water bath and dapped dry. Their weight (W_0) was recorded and the samples were placed onto a grid in a humidity chamber, held constant at room temperature and 35% relative humidity. The weight (W_t) was recorded over various time intervals and the weight change (ΔW) of each was calculated, according to formula 2. The water holding capacity was then calculated according to formula 3:

$$\text{Weight loss over time: } \Delta W = (W_0 - W_t) \tag{2}$$

Where W_0 is the weight of the fully soaked sample, and W_t is the weight loss of each sample at each recorded time interval.

$$\text{Water holding capacity} = [(W_0 - \Delta W)/ W_0]*100 \tag{3}$$

Where W_0 is the weight of the fully soaked sample, and ΔW is the weight loss over time.

III. RESULTS AND DISCUSSION

As expected, the samples showed great variability of their micro-structural parameters, depicted in the following section. Samples prepared with $CaCl_2$ as stabilizer had much smaller voids and less and smaller windows as compared to the samples with the same phase percentage based on with NaCl. Therefore, only the results of A90C are being reported.
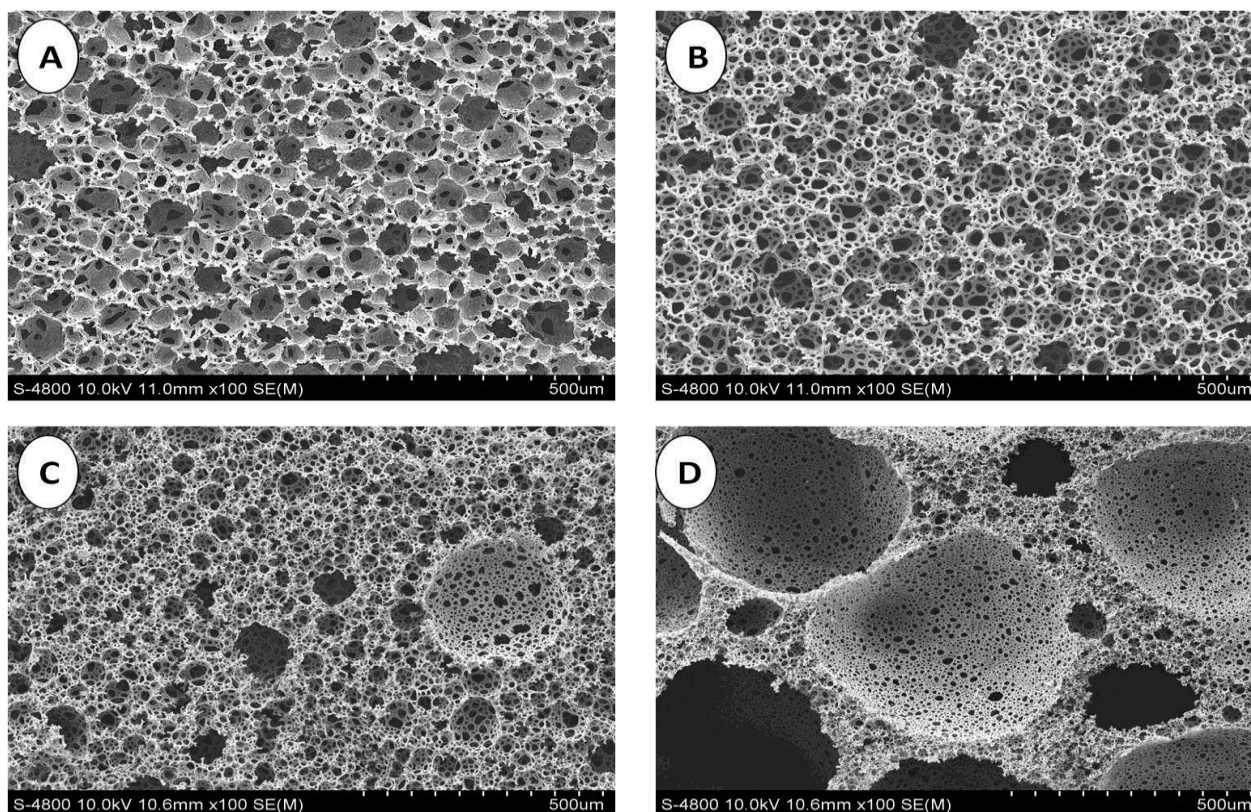
1. Morphological Characteristics

Fig. 1 SEM micrographs of the samples: (A) A90C, (B) A92N, (C) A94N, (D) A96N

SEM micrographs (Fig. 1) confirmed an increasing void size with increasing percentage of aqueous phase. Ranging from only 64-108 µm at 90% aqueous phase composition and $CaCl_2$ as stabilizer (A90C) up to 390-547 µm at 96% aqueous phase composition (A96N). Besides, the bigger size, a much more even distribution of windows was also found with increasing percentage of aqueous phase.

At low aqueous phase percentage, there were only very few windows, some of which were barely indicated but still closed, their size ranged from 8 - 33 µm. As the percentage of the aqueous phase increased, the number of interconnecting windows increased and their distribution became much more even throughout the entire void. The further increase of the percentage of the aqueous phase let to thinner cell walls in-between windows, which gave rise to a higher level of interconnectivity between adjacent voids, mostly due to Ostwald ripening [41]. At an aqueous phase percentage of 94%, coalescence between voids as well as windows could be observed. The windows of this sample were overall the largest with 15 - 32 µm. A further increase in the percentage of aqueous phase led to much larger voids, the average size of the

windows decreased to 3-22 μm, however, due to their much wider and even distribution, a higher level of interconnectivity could be obtained. It was found in the samples with varying ratio of S to DVB, that the pore size decreased with increasing DVB to S ratio.

The surface area of the samples initially decreased with increasing void size, however sample A96N had a surface area more than twice as high as the reference sample, A90N. This could be due to random polymerization of styrene with divinylbenzene, since both components were added simultaneously prior to the addition of an initiator [42,43]. The surface area of the samples with higher DVB content showed a much lower surface area compared to the reference sample.

2. Water adsorption capacity

It was found that the size of the voids and windows as well as the level of interconnectivity directly affected the water adsorption capacity of the PolyHIPE samples. With increasing void size and interconnectivity, the rate of adsorption as well as the maximum adsorption capacity increased significantly, as displayed in figure 2. Regardless the void size and interconnectivity, the water adsorption characteristics of all samples followed a similar pattern (except for sample A92N, which besides the quick rise in the beginning also showed a major increase in adsorption at the 60 minutes measurement); a rapid rate of adsorption within the first 1.5 minutes, followed by a slow, gradual increase until constant weight was reached after 5 days. However, the total amount of water adsorbed varied greatly. The sample with the smallest pores (A90C) was able to absorb only 8.16 times its own weight, followed by A90N with 10.23, and A92N with 12.61. Whereas the samples with the larger pores were able to absorb 16.69 (A94N), and 23.65 (A96N) times its own weight, respectively.
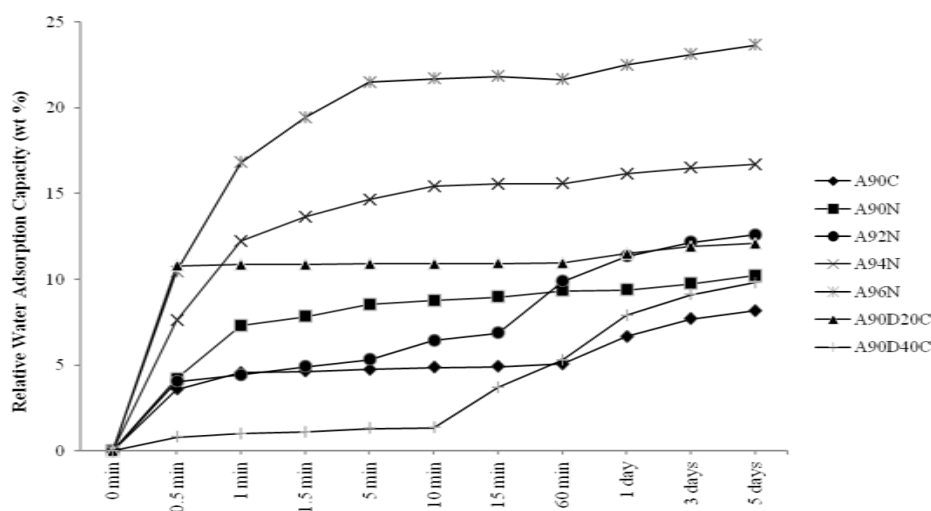

Fig. 2. Relative water adsorption capacities of Poly(S/DVB)HIPEs over time

3. Water holding capacity

Interestingly, the water holding capacity also increased with increasing void size. As shown in figure 3, the initial water loss after 1 day was of similar magnitude in all samples; 3.99% (A90C), 4.63% (A90N), 4.21% (A92N), 3.86% (A94N), and 3.71% (A96N) respectively for the samples with constant S to DVB ratio. The samples with higher DVB content had an overall lower water holding capacity, and the capacity decreased further with increasing DVB content. The decrease was most likely not only due to the smaller void size, but also to the more restricted swelling of the material, since the swelling of a material is dependent on the nature and concentration of crosslinking monomer [44]. However, after 2 weeks in the experiment, the samples with larger pores started to retain significantly more water than the samples with smaller voids. Samples A96N and A94N had only lost 25.62%, and 26.46% respectively, whereas the samples with smaller pores had lost between 32.78% (A92N) and 47.96% (A90D40C). This trend remained over the next weeks. After 4 weeks, the losses were 53.65% (A96N), 56.63% (A94N), 62.21% (A92N), 69.75% (A90N), 74.13% (A90C), 65.75%

(A90D20C), and 85.34% (A90D40C) respectively. After 6 weeks, the sample with smaller voids had lost almost all their water; 95.53% (A90N) to 99.9% (A90D40C), while the samples with larger voids still retained more than 20% of water. Their losses after 6 weeks were 88.26% (A92N), 81.12% (A94N), and 76.78% (A96N), respectively. The results suggest, a linear relationship between the water holding capacity and void size. Table 1 summarizes our findings.
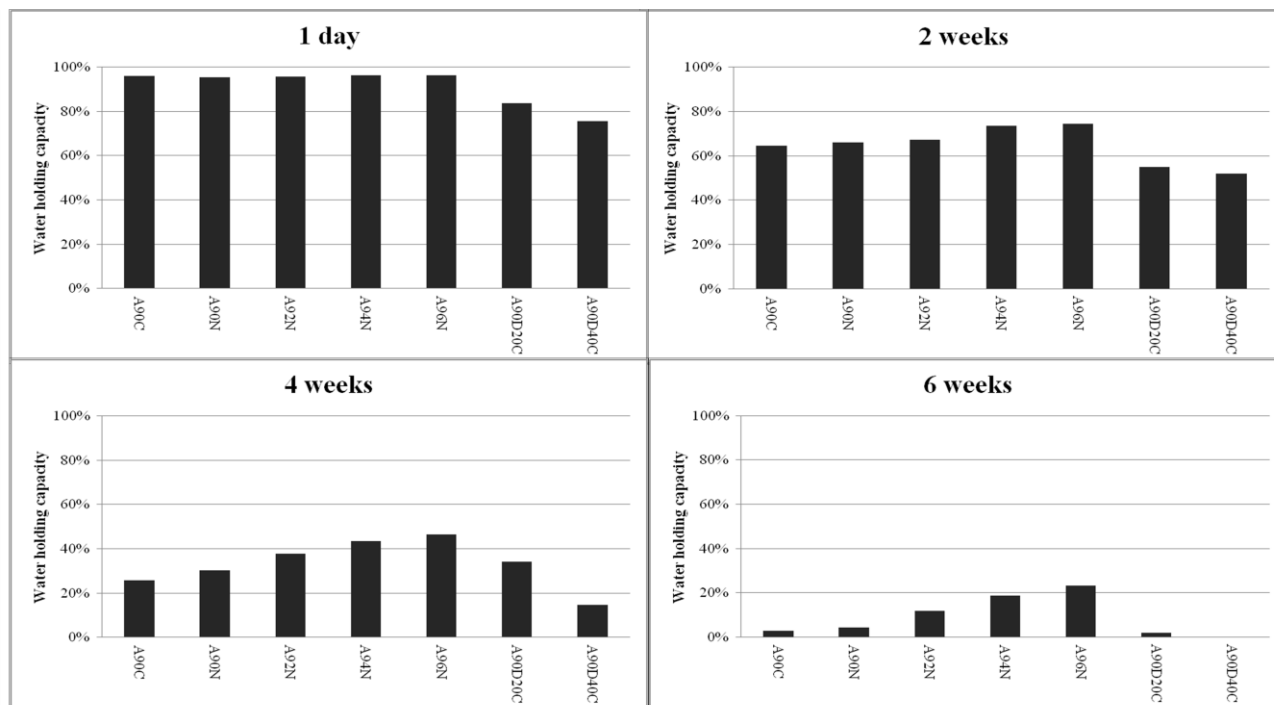

Fig. 3. Relative water holding capacities of Poly(S/DVB)HIPEs over time

TABLE I: SUMMARY OF MORPHOLOGICAL CHARACTERISTICS IN RELATION TO WATER ADSORPTION AND HOLDING CAPACITY

Sample	A90C	A90N	A92N	A94N	A96N	A90D20C	A90D40C
surface area (m^2)	24.147	23.612	21.847	18.005	50.582	8.585	9.474
void size (µm)	64-108	88-120	46-140	55-317	390-547	88-117	60-98
window size (µm)	8-33	6-35	10-34	15-32	3-22	6-29	23-29
WAC (wt. %, at equilibrium)	8.2	10.2	12.6	16.7	23.7	12.1	9.8
WHC (maximum number of days)	42	44	46	52	54	44	34

IV. CONCLUSION AND SUGGESTED WORK

This study showed a direct relationship between the void size and level of interconnectivity of Poly(S/DVB)HIPEs on water adsorption and holding capacities. As expected, the maximum amount of adsorbed water increased with increasing pore size, due to the availability of higher free void volume. Interestingly, the samples with larger voids were also able to hold on to the water for a much longer period of time as compared to the smaller voids. This suggests chemisorption between the pores of the monolith and the water particles. For a better understanding of the effect of porosity on water adsorption and holding capacity of PolyHIPEs, examination of the structure of the cell-wall would be

beneficial. Furthermore, the effect of the monomer used in the synthesis and possible further modifications to increase the hydrophilicity of PolyHIPEs should be investigated.

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