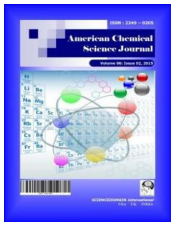

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Synthesis and Characterisation of PVA/PVOH Based Super Porous Hydrogel

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Authors' contributions

This work was carried out in collaboration between all authors. Author SKB designed the study, wrote the protocol and first draft of the manuscript. Author HS revised the manuscript and author SCM managed the analysis of the study. All authors read and approved the final manuscript.

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ABSTRACT

The present paper explains the synthesis of super porous hydrogel (SPH) with reinforcement of different concentrations (0.05, 0.1, 0.15 and 0.2 g) of PVA by solution polymerization. The polymerisation process is conducted at a pH value of 5. The corollaries of PVA on different characteristics of super porous hydrogel were studied. The characterization study involves measurement of apparent density, swelling, mechanical strength and microstructure. The PVA added SPH are treated for a total time of 550 minutes in double distilled water and acid salt solution to analyse the swelling properties. The result shows that inclusion of PVA to SPH reduces its swelling tendency culminating that; the empathy for swelling is more in double distilled water than acid medium.

Keywords: Super porous hydrogel; poly vinyl alcohol; apparent density; mechanical strength; swelling studies.

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ABBREVIATIONS

PVA - Poly vinyl alcohol
DDW - Double distilled water
SEM - Scanning electron microscope
FTIR - Fourier Transform infrared spectroscopy
ASS - Acidic salt solution
SPH - Superporous hydrogel
SPHHPs - Superporous hybrid hydrogels of PVA
SPHHP05 - Superporous hybrid hydrogel with PVA 0.05 g
SPHHP10 - Superporous hybrid hydrogel with PVA 0.1 g
SPHHP 15 - Superporous hybrid hydrogel with PVA 0.15 g
SPHHP 20 - Superporous hybrid hydrogel with PVA 0.2 g

1. INTRODUCTION

Hydrogels are water absorbing and cross-linked hydrophilic polymers, with a network structure, which are able to imbibe large amounts of water, and are water insoluble [1-3]. For the pharmaceutical applications they are used for controlled drug delivery, release control can be governed by both swelling and biodegrading properties [4-6]. The swelling properties of hydrogels are mainly related to the elasticity of the network, the presence of hydrophilic functional groups in the polymer chains, the extent of cross-linking, and porosity of the polymer. The physical characteristics of hydrogels including their swelling ratio also depend on the balance between attractive and repulsive ionic interactions and solvent mediated effects [7,8]. Owing to their high water affinity and biocompatibility, hydrogels based on poly (acrylic acid) and its derivatives [9,10] have attracted the attention [11-13]. They have been used for various biomedical, agricultural applications, for their absorbent properties, biodegradability and biocompatibility. The beginning of hydrogel dates back to the year 1960 when Wichterle and Lim first proposed the use of hydrophilic networks of polymer (2-hydroxy ethyl methacrylate) in contact lenses [14]. These are cross linked network of hydrophilic polymers but are insoluble in water. These swell too much larger size than the original one and still maintain a distinct 3D structure in swollen state. The characteristic water insoluble behavior is due to chemical or physical crosslinking which provide a network structure and physical integrity to the system [15]. Due to rigid crystalline structure and low elasticity in polymer chains, hydrogels swell very slowly and it may take a few hours to even days to achieve complete swelling. The slow swelling of hydrogels results from diffusion of water through glassy matrix of dried hydrogel. Though, the slow swelling of these hydrogels is useful in various applications but these are not applicable when faster swelling is required [16]. Therefore, a new generation of hydrogels i.e. Super porous hydrogels have been developed for this purpose. These are the hydrogels having interconnected pores of few hundred µm which swell to equilibrium size in a short period of time i.e. less than 20 minutes, to make them useful as gastro retentive device [17]. The interconnected pores lead to the formation of open capillary channels and fast swelling is achieved through capillary wetting of interconnected pores i.e. water is rapidly absorbed by capillary due to attractive forces within the pores. The present work explained the comprehensive outline of mechanical characteristics of super porous hydrogel fortified with PVA/PVOH.

2. MATERIALS AND METHODS

The materials used in the experiment for synthesis of super porous hybrid hydrogels are listed in Table 1. Acrylamide, N-N-methylene bisacrylamide (BIS), Span-80 and N-N-N´-N´-tetra methyl ethylene diamine were purchased from Loba chemical Pvt Ltd, Mumbai, India. Acrylic acid, Sodium hydrogen carbonate, Sodium hydroxide, Sodium chloride, Hydrochloric acid, Poly vinyl alcohol were purchased from SD Fine Chemical Ltd, Mumbai, India. Double distilled water (DDW) was prepared in our laboratory. Swelling study was conducted both in DDW and acid media. Acidic salt solution at pH value of 2 was prepared by dissolving 5.85 g of NaCl and 0.1 N HCl in DDW to make 1 litre solution.

Table 1. Batch ingredients for SPHHs

Raw materials	Composition in aqueous solution	Role in polymerization	SPH	SPHHP05	SPHHP10	SPHHP15	SPHHP20
Acrylamide	50% w/v	Monomer	6 ml	6 ml	6 ml	6 ml	6 ml
Acrylic Acid	50% v/v	Monomer	4 ml	4 ml	4 ml	4 ml	4 ml
BIS	2.5% w/v	Cross linker	2 ml	2 ml	2 ml	2 ml	2 ml
Span 80	10% v/v	Foam stabilizer	0.06 ml	0.06 ml	0.06 ml	0.06 ml	0.06 ml
TEMED	20% v/v	Catalyst	0.4 ml	0.4 ml	0.4 ml	0.4 ml	0.4 ml
DDW	_	Solvent	6.6 ml	6.6 ml	6.6 ml	6.6 ml	6.6 ml
PVA	Solid	Hybrid agent	_	0.05 g	0.1 g	0.15 g	0.2 g
5M NaOH	_	pH regulator	4.5 ml	4.5 ml	4.5 ml	4.5 ml	4.5 ml
Ammonium persulphate	20% w/v	Initiator	0.9 ml	0.9 ml	0.9 ml	0.9 ml	0.9 ml
$NaHCO_3$	solid	Foaming agent	4 g	4 g	4 g	4 g	4 g

3. SYNTHESIS PROCEDURE

All ingredients listed in Table 1 were added to the beaker except initiator and foaming agent. The pH of the reaction mixture was kept at 5 by carefully adding 5 molar NaOH drop by drop. The reaction mixture was vigorously shaken in order to achieve homogenous mixture. Finally initiator was added with successive addition of foaming agent and mixed with a spatula. The solution polymerization was carried out at room temperature which can range from 25℃ to 35℃. The polymerization was allowed to continue for a maximum time of 10 minute. The synthesized SPH were removed with the forceps then allowed to dry in oven at 60℃ for 4 days. The dried SPH were chopped and were stored in airtight container until further use.

4. RESULTS AND DISCUSSION

4.1 Scanning Electron Microscope Studies

The dried hydrogels were cut to expose their inner structure. The test was done on a small piece of hydrogel. The morphology and porous structures of the hydrogels were examined using Model JSM-5610 LV Scanning Electron Microscope (Japan) with an operating voltage of 15 kV. Figs. 1-2 are the SEM images of SPHHP20 under magnification of X100 and X35.

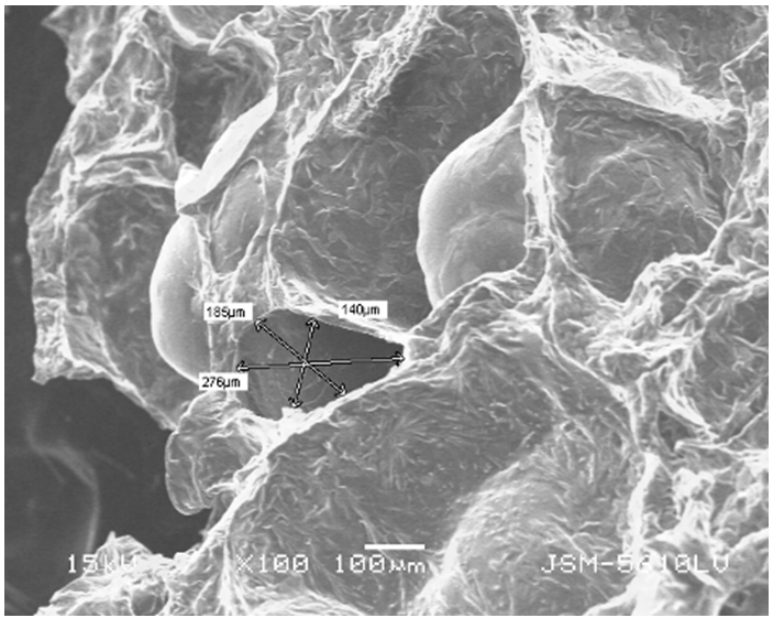

Fig. 1. SEM image of SPHHP20 under magnification of X100

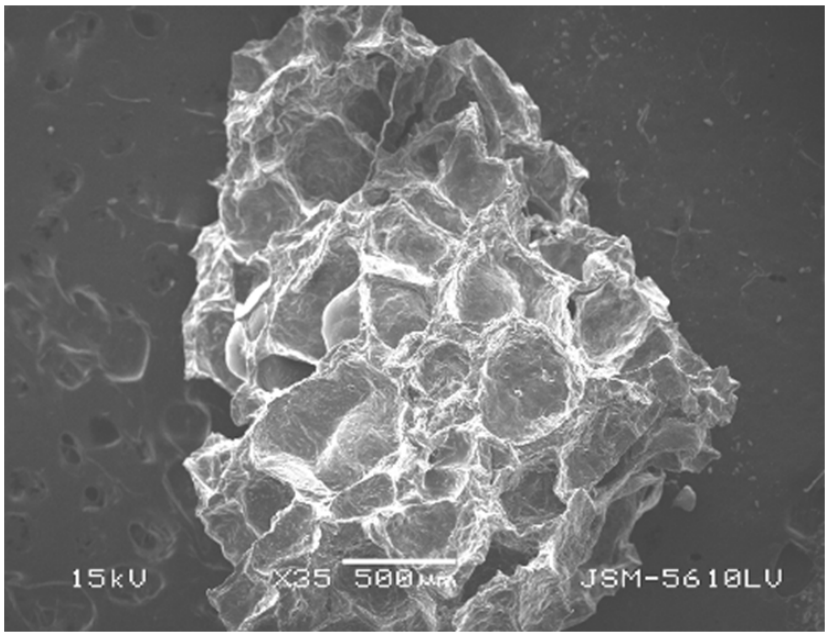

Fig. 2. SEM image of SPHHP20 under magnification of X35

4.2 FTIR Analysis for Hydrogel

Fig. 3 reveals the FTIR spectrum for SPHHP20. The test confirms the presence of different functional groups present in the hydrogel. FT-IR study was carried out using model Shimadzu 8400S (Japan) in the range of 400–4000 cm^{-1}.

The FTIR result shows the important peaks obtained. At peak 3466.2 which confirms the presence of N-H stretch, at peak 1562.39 confirms N-H bend and at peak 1464.02 confirms C-N stretch functional group from acrylamide and at peak 3045.7 confirms the presence carboxylic acid (OH stretch) functional group from acrylic acid.

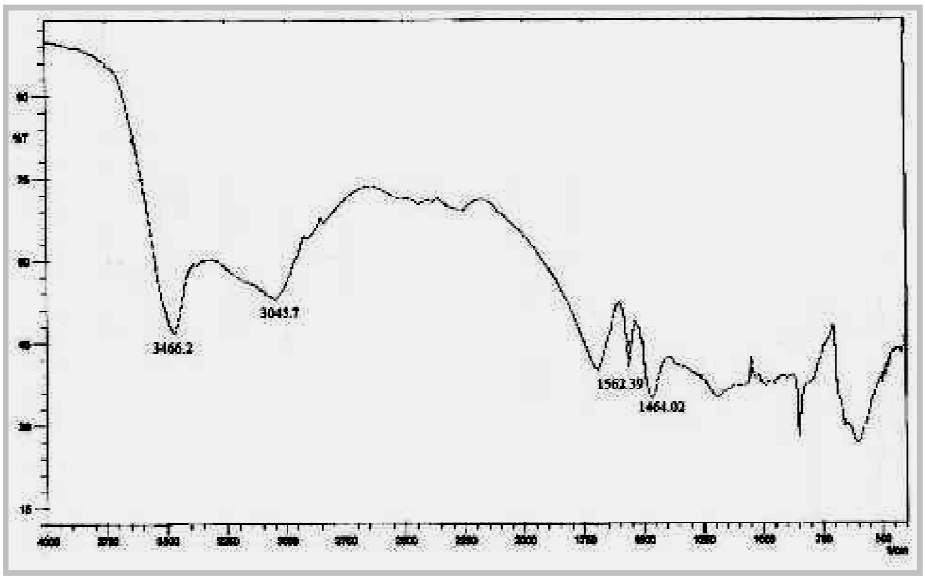

Fig. 3. FTIR spectrum for SPHHP20

4.3 Compressive Strength Studies for SPHHP

The above result shows that by adding small quantities of PVA the strength have increased drastically. From Table 2 it is observed that SPHHP20 can withstand more than five times penetration pressure than SPH.

4.4 Swelling Studies for Hydrogels

The swelling properties of hydrogels are mainly due to the presence of hydrophilic functional groups (such as -COOH, $-CONH_2$) in the polymer chains. In the experiment, swelling ratios has been examined for a total time duration of 550 minutes for each sample in DDW and ASS medium. Figs. 4-5 shows the variation of swelling ratio with time; for all samples in both mediums. The swelling ratio has been calculated from the equation-1.

Table 2. Compressive strength for SPH and SPHHP20

Sample name	Compressive strength $gf.cm^{-2}$
SPH	61.79
SPHHP20	317.6

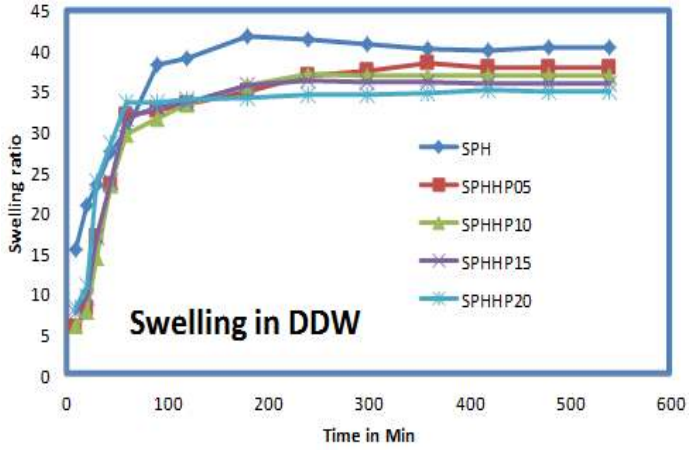

Fig. 4. Swelling curves of SPH and SPHHPs in DDW

$$Q = (W_s – W_d)/W_d \quad (1)$$

where, Q is the swelling ratio, W_s is the weight in the swollen state and W_d the weight in the dried state.

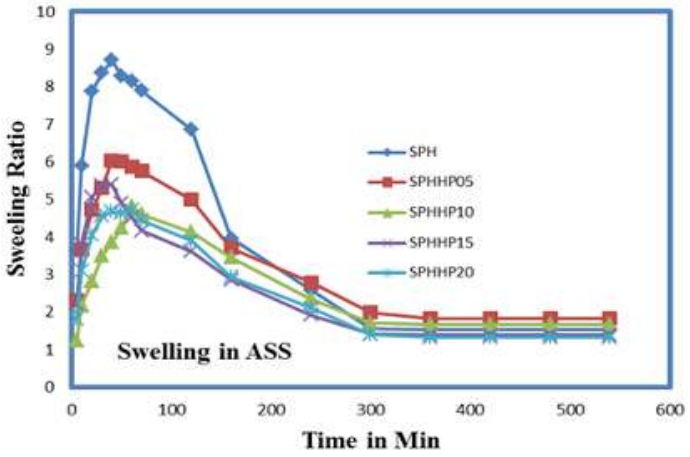

Fig. 5. Swelling curves of SPH and SPHHPs in ASS

From Fig. 4 it is observed that the prepared SPHHPs have high water absorbing capacity. The maximum swelling ratio decreases with the increase in amounts of PVA; might be due to entanglement with the cross-linked PVA network and for the decrease in flexibility of the polymeric chains. Bonds between PVA and P (AA-co-AM) reduced the ability of the polymer to form hydrogen bonds with water molecules, thus limiting its water absorption. The maximum swelling in ASS has been achieved within 40 to 60 minutes. Hereafter the de swelling process has been started. The extent of swelling is very high in DDW compared to ASS. For SPHHP10 maximum swelling ratio observed is 36 in DDW and that in ASS it is 5. Fig. 5 reveals that maximum swelling ratio for SPHHPs gets reduced around 5 to 8 times in acidic salt solution than that of doubled distilled water; this winds up that; the bloating of SPHHPs are highly affected by the swelling media pH and its salt content.

4.5 Density Measurements for Hydrogels

The density measurements of hydrogels shows that the density of SPHHPs is lower compared with the SPH. The density of SPHHPs decreases with increase in PVA amounts. Detailed apparent densities of SPH and SPHHPs samples are presented in Table 3. After PVA was mixed with the monomer solution, it swelled up; so that monomers and cross linker were absorbed into the cellulose network. After polymerization was complete, the cellulose network of PVA particulates and the cross-linked poly (AA-co-AM) networks formed. Increased concentration of PVA might be prevented the bubbles in it to escape from the solution mixture and thus increasing the porosity of SPHHPs and hence decreasing density. The SPHHPs have the density lower than both the swelling media and thus floats in it.

Table 3. Apparent densities of SPH and SPHHPs samples

SPH and SPHHP samples	Apparent density $g.cm^{-3}$
SPH	0.785
SPHHP05	0.764
SPHHP10	0.742
SPHHP15	0.725
SPHHP20	0.711

5. CONCLUSIONS

SPHHPs were prepared from solution polymerization at various amounts of PVA. It is observed that SPHHPs are porous in structure. The presence of functional groups such as (-OH, -COOH and $-CONH_2$) are responsible for swelling and deswelling of the hydrogels. The robustness of SPH is comparatively poor; the presence of PVA improved mechanical strength, which prevents the breakage of SPHHPs by improving mechanical stability. The swelling ratio and size of SPHHPs decreased with the increase in PVA content in both DDW and ASS. It is noteworthy to dissolve that; the swelling ratio of the SPHHPs was found to be pH dependent with varying amounts of PVA inclusion.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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