https://doi.org/10.31436/iiumej.v62i1.3236

SOLAR-DRIVEN WATER PURIFICATION: ADVANCING PVA-CHITOSAN/PANI HYDROGEL TO ENHANCE SOLAR VAPOR GENERATION FOR FRESHWATER TREATMENT

FLORA SERATI[1], SYAZWANI MOHD ZAKI[2*],
AHMAD AKID ZULKIFLI[2], SITI RABIZAH MAKHSIN[3]

[1]Department of Electrical and Computer Engineering, Kulliyah of Engineering, International Islamic University Malaysia, PO Box 50728 Kuala Lumpur, Malaysia.
[2]Department of Manufacturing and Materials Engineering, Kulliyah of Engineering, International Islamic University Malaysia, PO Box 50728 Kuala Lumpur, Malaysia.
[3]Micro-Nano ElectroMechanical System Lab (MiNEMS Lab), School of Mechanical Engineering, College of Engineering, University Technology MARA, 40450, Shah Alam, Selangor, Malaysia.

**Corresponding author: syazwani_mohdzaki@iium.edu.my*

(Received: 26 March 2024; Accepted: 18 June 2024; Published online: 10 January 2025)

ABSTRACT: Water scarcity is a global issue that affects human beings' ability to live healthily, and immediate action must be taken to alleviate this issue. Despite advances in water purification, current technologies exhibit pronounced deficiencies. Existing filtration systems and other conventional methods remain energy-intensive, with escalating maintenance costs at large-scale production. The advancement of innovative materials holds significant potential to revolutionize the landscape of solar water purification. While conventional solar vapor generation (SVG) technology has faced challenges in achieving high water yields under natural sunlight conditions, innovating new materials can substantially reduce the energy requirements for water vaporization. Herein, we introduce our outstanding light-absorbing hydrogel consisting of polyvinyl alcohol (PVA) and chitosan (CS) as the substrate with the addition of polyaniline (PANi) as the light absorber for water evaporation via SVG technique. In this study, PVA-CS/PANi hydrogels were prepared with distinct concentrations of PVA and denoted as PVA-CS/PANi/1.3 mol.%, PVA-CS/PANi/2.7 mol.% and PVA-CS/PANi/3.9 mol.%. Copolymerization of PVA-CS hydrogels with PANi was conducted via solution polymerization to incorporate PANi into the hydrogel network structure. Incorporating light-absorbing materials, such as PANi, into the hydrogel network structure is expected to enhance the absorption properties. The morphological structure of the obtained hydrogels was analyzed by scanning electron microscopy (SEM). In contrast, the physicochemical and mechanical properties of the hydrogels were evaluated by dynamic light scattering (DLS), FTIR, swelling test and rheology. From the analysis demonstrated in this work, the structure of PVA-CS/PANi hydrogels is significantly influenced by the concentration of PVA. The hydrogels' diameter and polydispersity index (PDI) were 146 nm and 0.331, respectively. The storage modulus (G') of PVA-CS/PANi/3.9 mol.% depicted the highest value of 2356 Pa compared to PVA-PVA-CS/PANi/1.3 mol.%, which depicted the G' value of 1173 Pa. From FTIR analysis, the absorption band was found between 3600 to 3000 cm^{-1}, attributed to O-H and N-H groups of PVA and PANi, while the PVA-CS with the presence of PANi shows characteristic bands at 1620 cm^{-1}, 1508 cm^{-1}, and 1298 cm^{-1}. The microporous structure of PVA-Chitosan/PANi hydrogels increases with a higher concentration of PVA, demonstrating the degree of cross-linking of PANi, which contributes to the rigid structure of porous hydrogel. The influence of PVA concentration on the hydrogel's porous structure and surface area allows for greater dye adsorption. As demonstrated by PVA-CS/PANi/3.9 mol.%, it shows higher absorption of Methylene Blue (MB) into the structure. The performance of SVG using PVA-CS/PANi/3.9 mol.% hydrogels was measured, and the efficiency was found to be 69.8% under 1 sun with efficient temperature distribution on the surface. This finding indicates the capability of PVA-Chitosan/PANi/3.9 mol.% hydrogels in generating multi-scattering effects of natural sunlight for high-efficiency light-to-heat conversion via SVG.

ABSTRAK: Kekurangan air adalah isu global yang menjejaskan kehidupan manusia untuk hidup sihat, dan tindakan drastik perlu diambil bagi mengatasi masalah ini. Walaupun terdapat kemajuan dalam pembersihan air, kelemahan ketara masih wujud dalam teknologi semasa. Sistem penapisan sedia ada dan kaedah konvensional lain kekal menggunakan tenaga dengan intensif, di tambah kos penyelenggaraan yang tinggi pada pengeluaran berskala besar. Pembangunan bahan inovatif mempunyai potensi besar bagi merevolusi pembersihan air dengan suria. Walaupun teknologi penjanaan wap suria konvensional (SVG) sedang menghadapi cabaran dalam mencapai hasil air yang tinggi di bawah keadaan cahaya matahari semula jadi, inovasi menggunakan bahan baharu dapat mengurangkan keperluan tenaga dengan berkesan bagi tujuan pengewapan air. Di sini, kami memperkenalkan hidrogel penyerap cahaya yang terdiri daripada polivinil alkohol (PVA) dan kitosan (CS) sebagai substrat dan dengan penambahan polianilin (PANi) sebagai penyerap cahaya bagi penyejatan air melalui teknik SVG. Kajian ini mensintesis hidrogel PVA-CS dengan penambahan PANi dengan kepekatan PVA berbeza; Hidrogel PVA-CS dengan PANi ditandakan sebagai PVA-CS/PANi/1.3 mol.%, PVA-CS/PANi/2.7 mol.%, dan PVA-CS/PANi/3.9 mol.%. Hidrogel PVA-CS dengan kopolimer PANi telah disintesis dengan pempolimeran larutan bagi meresapi PANi ke dalam struktur rangkaian hidrogel. Dengan mengadaptasi material penyerap cahaya seperti PANi ke dalam struktur rangkaian hidrogel, diharapkan dapat membantu dalam penyerapan. Struktur hidrogel yang diperolehi telah dicuba dari segi morfologi (SEM), sifat fisiokimia dan mekanikal (DLS, FTIR, ujian bengkak dan reologi). Melalui analisis ini, kepekatan PVA mempengaruhi struktur hidrogel PVA-CS/PANi dengan ketara. Diameter hidrodinamik hidrogel PVA-Chitosan yang dihasilkan ditentukan oleh DLS. Diameter dan indeks polidispersi (PDI) didapati masing-masing 146 nm dan 0.331. Modulus penyimpanan hidrogel PVA-CS untuk semua sistem ditentukan oleh reologi. Modulus penyimpanan (G') PVA-CS/PANi/3.9 mol.% mempunyai nilai tertinggi 2356 Pa berbanding PVA-PVA-CS/PANi/1.3 mol.% sebanyak G' 1173 Pa. Melalui Analisis FTIR, jalur serapan didapati antara 3600 hingga 3000 cm-1, dikaitkan dengan kumpulan O-H dan N-H PVA dan PANi manakala PVA-CS dengan kehadiran PANi menunjukkan jalur ciri pada 1620 cm-1, 1508 cm-1, dan 1298 cm-1. Struktur liang mikro hidrogel PVA-Chitosan/PANi meningkat dengan kepekatan PVA tertinggi menunjukkan bahawa tahap pengikatan silang PANi memberikan struktur hidrogel berliang lebih tegar. Pengaruh kepekatan PVA pada struktur berliang hidrogel dan luas permukaan membolehkan penyerapan pewarna lebih tinggi seperti ditunjukkan oleh PVA-CS/PANi/3.9 mol.%, menunjukkan penyerapan Metilena biru (MB) lebih tinggi ke dalam strukturnya. Penggabungan bahan penyerap cahaya, seperti PANi kepada formulasi hidrogel boleh meningkatkan sifat penyerapannya. Prestasi SVG menggunakan hidrogel PVA-CS/PANi/3.9 mol.% diukur, didapati sebanyak 69.8% di bawah 1 matahari dengan taburan suhu yang cekap pada permukaan hidrogel. Dapatan kajian ini menunjukkan keupayaan hidrogel PVA-Chitosan/PANi/3.9 mol.% dalam menjana pelbagai taburan cahaya matahari semula jadi bagi menukar cahaya kepada haba yang cekap melalui SVG.

KEYWORDS: *Hydrogel, solar vapor generation, polyaniline, polymer colloids*

1. INTRODUCTION

Water is an essential element in maintaining life and is needed for the survival of all organisms. Water resources are critical assets, so water conservation is imperative since the global water crisis has become a common phenomenon. According to the United Nations Development, more than 40% of people are affected by water scarcity, an alarming number expected to increase as temperatures rise. Since 1990, 2.1 billion people have improved their water sanitation, yet depletion of drinking water resources remains across all continents. Many nations suffer from water scarcity, and rising drought and desertification aggravate these circumstances. It is predicted that by 2050, at least one in four individuals will experience recurring water shortages [1]. The difficulty of maintaining sustainable levels of water use is expected to increase because of rising population pressure, changing water consumption habits, and climate change. This is followed by the rising number of heavy metals in natural resources resulting from industrialization and the improper discharge of wastewater into freshwater. Solar energy is the most abundant and renewable energy on earth. Therefore, it is vital to maximize the use of solar energy for sustainable future development to protect the planet. One of the technologies that can efficiently utilize solar energy is Solar Vapor Generation (SVG). SVG is a technology for purifying polluted water through solar energy evaporation by separating water from impurities and, similar to the natural hydrological cycle, replenishing freshwater on land [2]. It is a famous alternative to producing water for living things to survive. In SVG, two main components require improvement to facilitate more efficient water evaporation. These two main components are the light absorber material and the substrate. The light absorber material is essential to improve the light-to-heat conversion during the SVG process, and it is also known as photothermal-conversion material. Ideally, black materials with low transmittances, such as carbon nanomaterials, are ideal light absorbers for incident light with a broad range of wavelengths. For high-efficiency SVG design, the substrate material, such as the light absorber, is important. In contrast, the substrate material must perform two basic things: water transport/evaporation and thermal insulation. Other factors, such as good wetting properties and continuous pathways, are important for water to flow and evaporate efficiently. Besides, for SVG, low thermal conductivity and porous structures are needed to achieve better thermal insulation. The ratio of the thermal energy contained in the generated vapor to the incoming solar flux can be used to calculate the evaporation efficiency [3].

$$\eta = \frac{\dot{m}\, h_{LV}}{P_{in}} \tag{1}$$

where $\dot{m}$ is denotes the mass flux, h_{LV} is the total enthalpy of liquid-vapor transformation, and P_{in} is the rate of solar energy incident. The marking point as an ideal number to achieve highly efficient SVG is $1\mathrm{kWm}^{-2}$ (typically ~50% to higher than 80%) under 1 sun or even weaker natural daylight.

In recent years, there has been an increasing interest in SVG involving distinct hydrogels owing to the network structure that can absorb a significant amount of water. Hydrogels are hydrophilic polymer chains that form networks, have specific water states, and are swollen by dispersion mediums such as water. The floatable composite hydrogel possesses these characteristics, permitting the gels to effectively heat the water's surface while it undergoes evaporation, resulting in a higher efficiency of water evaporation. Hydrogel has become a trend in SVG technology and is still in its early stages. Owing to outstanding properties such as water-transporting material due to its strong hydrophilicity and ability to bond with water easily, the hydrogel is the best selection for the SVG platform. In comparison to natural polymers, the biological activity of the hydrogel produced by synthetic polymers is diminished [4]. Natural and synthetic polymers can be combined during manufacturing to produce hydrogels with the desired physical and chemical properties. In the previous study conducted by Khurma et al.[5], he developed semi-interpenetrating chitosan and PVA-crosslinked Genipin hydrogels. In that work, the study was conducted at various pH levels, temperatures, and swelling behaviours to investigate the properties of the hydrogels. According to the results obtained in our study, the correlation between PVA concentration and swelling capacity is interesting, as the concentration of PVA must be greater than the concentration of chitosan to enhance the swelling capacity of PVA-CS hydrogel. The most remarkable result from this study is that at the maximum concentration of PVA, the PVA-CS hydrogel has demonstrated a higher ratio of OH groups to NH_2 groups. This finding suggests that some OH groups not involved in hydrogen bonding can attract more water, resulting in higher swelling ability. However, in a similar swelling investigation by Khan et al. on PVA-CS hydrogels crosslinked by UV light, the opposite trend was observed regarding swelling behaviour [6]. That research observed greater swelling ability in the hydrogels containing more chitosan. This difference in swelling trajectory may be attributed to the method used to crosslink the hydrogels. Khan's group utilized UV radiation crosslinking, resulting in a complete chitosan and PVA hydrogel network. Due to the temperature sensitivity of the hydrogel, the difference between these two results is owing to the percentage hydrolysis of PVA used by Khurma et al. The increase in frozen water is attributed to the increased hydrophilicity of the hydrogels, which was induced by the addition of PVA. Another study conducted by Guo et al. [2] on in situ gelation of PVA with uniform nanoparticles of titanium sesquioxide (Ti_2O_3) exhibited high photothermal conversion efficiency of up to 90%. They conducted experiments with various concentrations of PVA, which resulted in different evaporation rates depending on the concentration of PVA. However, the optimal results are independent either on the highest concentrations of PVA or the lowest concentration; instead, they are connected to other factors such as light absorber materials. The SVG system can be improved by adding light absorber materials to the substrate, as demonstrated in a study conducted by Yin et al.[7]. In that work, a novel porous double-network hydrogel (p-PEGDA-PANi) reportedly achieves a maximum solar thermal efficiency of 91.5%. The pristine hydrogel by itself has poor thermal conductivity. Still, when combined with PANi as a composite and given the porous structure, it can effectively confine heat transfer to the evaporating surface and reduce heat loss to bulk water. Moreover, after PANi cross-linking took place, the porous hydrogel sample exhibited a broader and stronger absorption (98.5%) juxtaposition to the pure PEGDA samples, especially in the visible and near-infrared (NIR) regions, confirming the strong absorption capacity of PANi for SVG application.

In this work, PVA-CS/PANi hydrogels were prepared with distinct concentrations of PVA and denoted as PVA-CS/PANi/1.3 mol. %, PVA-CS/PANi/2.7 mol.% and PVA-CS/PANi/3.9 mol.%. Copolymerization of PVA-CS hydrogels with PANi was conducted via solution polymerization to incorporate PANi into the hydrogel network structure. Incorporating light-absorbing materials, such as PANi, into the hydrogel network structure is expected to enhance the absorption properties. The morphological structure of the obtained hydrogels was analyzed by scanning electron microscopy (SEM). In contrast, the physicochemical and mechanical properties of the hydrogels were evaluated by dynamic light scattering (DLS), FTIR, swelling test, and rheology. From the analysis demonstrated in this work, the structure of PVA-CS/PANi hydrogels is significantly influenced by the concentration of PVA and the ability of the hydrogels to generate multi-scattering effects of natural sunlight for high-efficiency light-to-heat conversion via SVG.

2. MATERIALS AND METHODS

2.1. Materials

Materials used for this experiment are 0.32 M aniline monomers, 0.08 M ammonium persulfate (APS), hydrochloric acid (HCl,1M), deionized water (DI), polyvinyl alcohol (PVA) powder, 0.44 mol% of chitosan (CS) powder, Acetic acid (glacial), calcium carbonate powder ($CaCO_3$), glutaraldehyde [GA, 50 wt% in deionized water], 150 ml distilled water, and 50 ml

N-Methyl-2-Pyrrolidone (NMP). The chemicals were purchased from Sigma-Aldrich and R& M Chemicals.

2.2. Method

The water bath was heated up to a constant temperature of 80°C. The PVA powder (1.3 mol.%, 2.7 mol.%, 3.9 mol. %) was gradually added to the heated reactor containing 150 ml of DI water, followed by CaCO3 powder added to the mixture. Subsequently, the solution was stirred vigorously for 2 hours. Then, 1.5 g of CS powder was dissolved in 0.4M acetic acid and stirred for 5 hours at 70°C. The CS solution was gradually added to the PVA solution and vigorously stirred for another 6 hours. After 6 hours, the solution was transferred to another beaker and cooled to room temperature. The milky-white PVA-CS solution was formed. Subsequently, 1M HCl was added to the solution, and the milky-white solution turned into a transparent solution, which was left for another 2 hours. The prepared polyaniline (PANi) powder was mixed with 50 ml N-Methyl-2-pyrrolidone (NMP) to dissolve the PANi powder. The mixture was then stirred for 1 hour. Next, the PANi-NMP solution was added to the PVA-CS/HCl solution, resulting in a mixture ready for hydrogel gelation. Glutaraldehyde (GA) [50 wt.% in DI water] 0.48 wt.% was added to 3 ml of the PVA-CS/PANi hydrogel solution, and the gelation process was left to occur for 24 hours.

2.3. Characterizations

The hydrodynamic diameter measurements were carried out using dynamic light scattering (DLS) (Zetasizer Nano S, Malvern Instruments, Malvern, UK). The PVA-CS solution sample was diluted to 0.1% w/w, and data were averaged over three consecutive runs at 25°C. The total solid content (TSC) was determined after the fabrication of PVA-CS solutions. To measure the TSC percentage, the mass of the boat dish and three different masses of the solution were recorded and labeled accordingly before allowing the prepared solutions to dry for 24 hours at 60°C. Fourier-transform infrared spectroscopy (FTIR) characterizations were performed using the Bruker Invenio. The FTIR spectra were measured within a spectrum range of 4000 – 700 cm-1 over 32 scans with a resolution of 4 cm-1. The PVA-CS/PANi hydrogel was freeze-dried for 72 hours before observation. Scanning Electron Microscope (SEM) (JEOL JSM5600) was utilized to observe the morphology and microstructure of the samples. The PVA-CS/PANi hydrogels were freeze-dried for 72 hours before observation. The mechanical properties of PVA-CS/PANi hydrogels were determined using a rheological experiment (Rheometer Anton Paar MCR) using a parallel plate in the amplitude and frequency sweep mode. The swelling capacity of PVA-CS/PANi hydrogels was determined using a swelling test. The PVA-CS/PANi hydrogels were immersed in a buffer solution (pH 4, pH 7, pH 10) and allowed them to swell until they reached equilibrium at regular time intervals for 24 hours. The absorption spectra of the Methylene Blue (MB) solution were measured by observing the absorption of contaminants by the PVA-CS hydrogels. The measurements were conducted at λ=665 nm using a spectrophotometer (SHIMADZU UV-1900, Tokyo, Japan), with the blank as a reference. The solar simulator lamp (Ossila Solar Simulator) in the laboratory setting simulates one sun illumination (100 mW/cm2) for the PVA-CS/PANi hydrogel and PVA-CS hydrogel efficiency test. The infrared thermal camera was employed to record the sample's heating process under a solar simulator lamp to investigate the maximum temperature distribution on the top surface of the sample.

3. RESULTS AND DISCUSSION

3.1. DLS Size Distribution

DLS measurement of PVA-CS hydrogels is depicted in Figure 1, which shows PVA hydrogels with a bimodal distribution of average particle diameter. This graph showed that the z-average diameter measured was 146nm with slightly aggregated particles. The aggregation of particles in the PVA-CS solution is influenced by the presence of a small amount of chitosan due to flocculation. PDI value indicates the size distribution of particles in a sample. The PVA-CS hydrogel has a low PDI of 0.331, suggesting that the sample is homogeneous, with most of the particles being of similar size. The findings demonstrate that the PVA-CS solution possesses suitable characteristics for solar absorption capacity owing to its smaller particle size, good stability, and mechanical strength. The system will be evaluated further with various PVA concentrations. Homogeneous dispersion of PVA-CS hydrophilicity in water requires a small particle size (nanoparticle) to prevent aggregation from occurring.

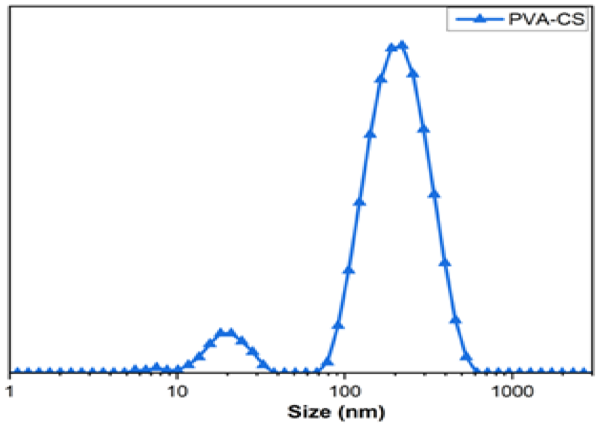

Figure 1. Particle size distribution of PVA-CS particles obtained from DLS analysis.

3.2. Total Solid Content (TSC) of PVA/Chitosan Solution

The total solid content (TSC) was conducted after the preparation of the PVA-CS solution. To measure the percentage of TSC, the mass of the boat dish and three different masses of the solution were recorded and dried in the oven for 24 hours at 60°C. The TSC data obtained is shown in Table 1. The TSC value of PVA-CS/PANi-3.9 mol.% was determined to be 87%, which is the highest percentage of all three observations. The magnitude of this value is sufficiently large to induce the polymerization of the solution into a hydrogel. Moreover, a low TSC value would result in an extended gelation period unfavorable for large-scale production. TSC influences the physical properties of hydrogel because hydrogel exhibits a denser microstructure when it has higher TSC values. Additionally, the TSC value would also impact the distribution of particles within the hydrogel. A previous study also found that an emulsion polymerization with a TSC value of 46% exhibited greater stability[8], and when the TSC value is below 20%, the hydrogel's overall strength may be diminished. Hence, a TSC value exceeding 46% is necessary and ideal for the synthesis of hydrogel[9].

Table 1. The total solid content of different concentrations of PVA-CS solution

PVA concentrations	Total Solid Content (%)
1.34 mol.%	72.5
2.7 mol.%	78
3.9 mol.%	87

3.3. Physical Observations of PVA-CS/PANi Hydrogels

The combination of PVA with chitosan results in a composite material that incorporates characteristics that impart mechanical robustness and stability, as well as tailoring the property of interest. PVA enhances the strength of the chitosan hydrogel and protects it against deterioration or degradation in aqueous environments. PVA is renowned for its exceptional characteristics that enhance the hydrogel matrix and its structural integrity. This characteristic is crucial for applications that necessitate the hydrogel's capacity in SVG applications that may be exposed to prolonged sunlight. Hence, this study presents the observation of PVA-CS hydrogels with different PVA concentrations, as depicted in Figure 2 (a-f). The appearance of the gel may be affected by the concentration of the PVA-CS hydrogel. In addition, the PVA-CS/1.3 mol.% exhibited a higher susceptibility to breakage upon contact, whereas higher concentrations of PVA-CS resulted in a stronger and more durable hydrogel. The polymer component ratio of PVA influenced these viscoelastic properties of PVA-CS hydrogel. Furthermore, Figure 2(d-f) shows the PVA-CS/PANi composite with varying concentrations of PVA. The color changes of PVA-CS/PANi are caused by the chemical reactions induced by the oxidation of PANi. The PANi concentrations are constant in this experiment. The hydrogel exhibited varying appearances depending on the concentrations of PVA, which consequently led to a more durable hydrogel. The presence of the dark hydrogel in PVA-CS/PANi/3.9 mol.% is necessary for the SVG application as a dark hydrogel has a higher capacity to absorb solar energy efficiently.

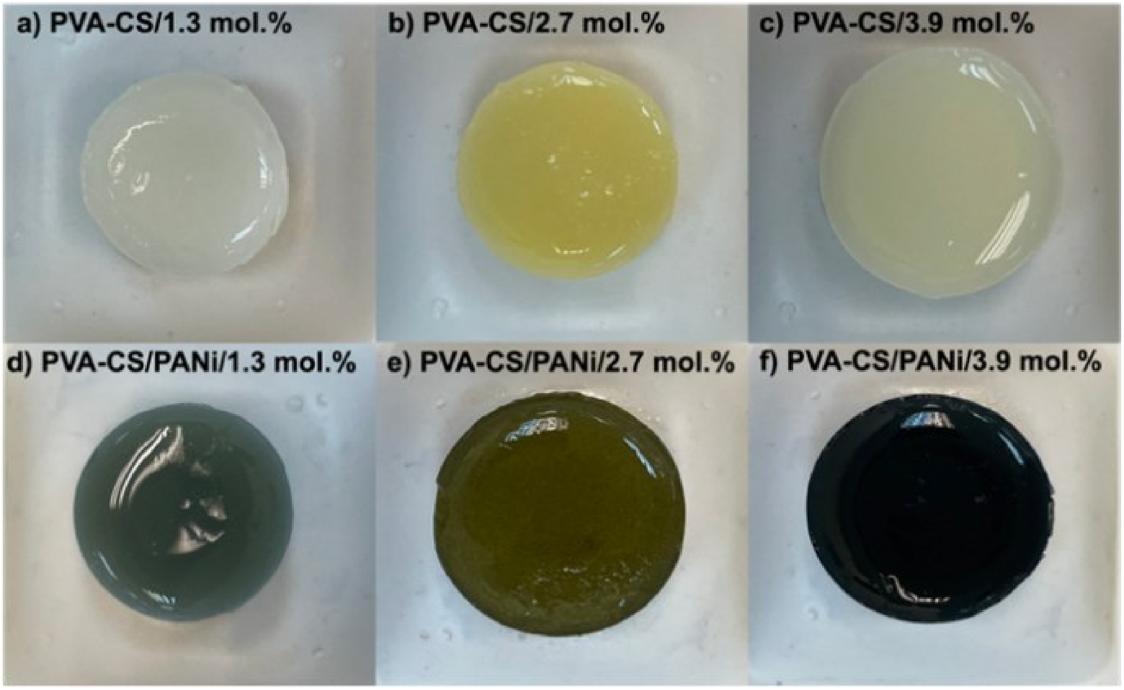

Figure 2. Gel images of PVA-CS hydrogel and PVA-CS/PANi hydrogel.

3.4. FTIR of PVA-Chitosan Hydrogel with Polyaniline

The FTIR spectra of PVA-CS hydrogel and PVA-CS/PANi hydrogel are depicted in Figure 3. It was observed that a broad peak at 3268 cm^{-1} corresponds to hydrogen bonding in PVA-CS hydrogel. The peak at 1665 cm^{-1} is typically associated with the carbonyl stretching vibration of the carboxylate group (-COO-) present in the chitosan structure. The PVA-CS with the presence of PANi exhibits peaks at 1620 cm^{-1}, 1508 cm^{-1} and 1298 cm^{-1}. These bands correspond to the C=N and C=C stretch for the quinoid and benzenoid structures of PANi.

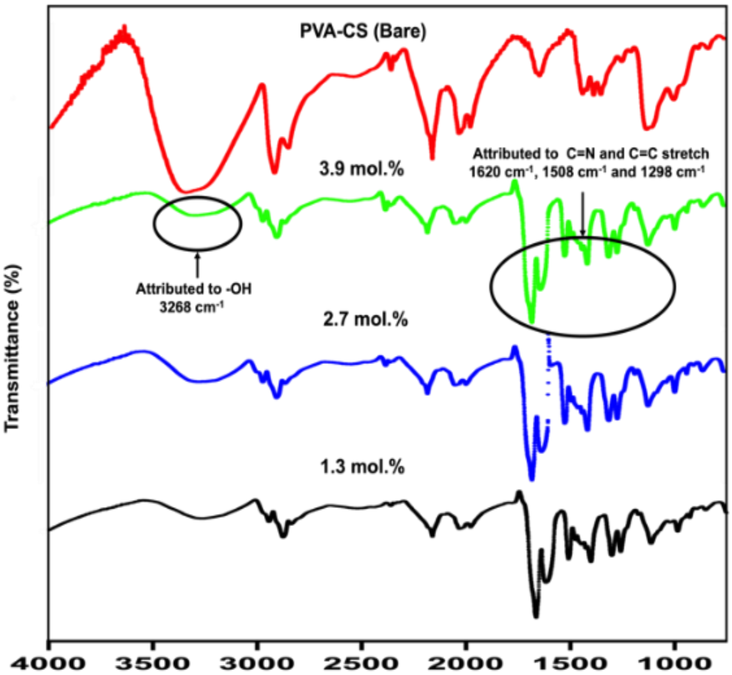

Figure 3. FTIR spectra of the chemical compositions of PVA-CS hydrogel and PVA-CS/PANi hydrogel

3.5. PVA-CS hydrogel and PVA-CS/PANi hydrogel SEM morphology

The SEM images were used to observe the cross-sectional morphology and microstructure of PVA-CS/PANi hydrogels with varying PVA concentrations (1.3 mol.%, 2.7 mol.%, 3.9 mol.%) and compared to PVA/Chitosan with PANI incorporation. Figure 4(a-f) displays the SEM morphology of the cross-section of the hydrogel at high magnification. Figure 4(a) illustrates the morphology of PVA-CS/1.3 mol.%, with fewer interconnected pores due to a lower polymer concentration. Fewer polymer concentrations may lead to a denser network, and PVA, being a hydrophilic polymer, is responsible for improving the hydrogel's viscosity. The PVA-CS solution decreased due to a lower PVA concentration. A decrease could induce restriction of polymer chain entanglement during the gelation process, thereby reducing the interconnected pores in the hydrogel. This can be seen in Figure 4(b-c), which displays a denser morphology with interconnected pores. The variation in PVA concentrations may lead to different hydrogel morphologies, and the presence of a denser morphology with interconnected pores may contribute to the mechanical strength of the hydrogel [10].

Furthermore, Figure 4(d-f) exhibits the SEM morphology of PVA-CS hydrogel incorporated under PANi with the influence of PVA concentrations. Adding PANi can impact the pore morphology and distribution within the hydrogel compared to pure PVA-CS hydrogels. Figure 4(d-f) demonstrates the distribution and dispersion of PANi within the PVA-CS hydrogel matrix, where particles or aggregates are visible as distinct features, and their distribution may enhance the homogeneity of the composite material. The microporous structure's pore size increases with the rise in PVA concentration, which is necessary for the PVA-CS/PANi hydrogel to provide a continuous water supply to the hydrogel's surface for SVG application. The pore distribution of the hydrogel indicates homogeneous gelation throughout the hydrogel matrix. The rich porous structure also enhances the multi-scattering of incident natural sunlight, enabling the incident light to be converted into heat at the evaporating surface[3].

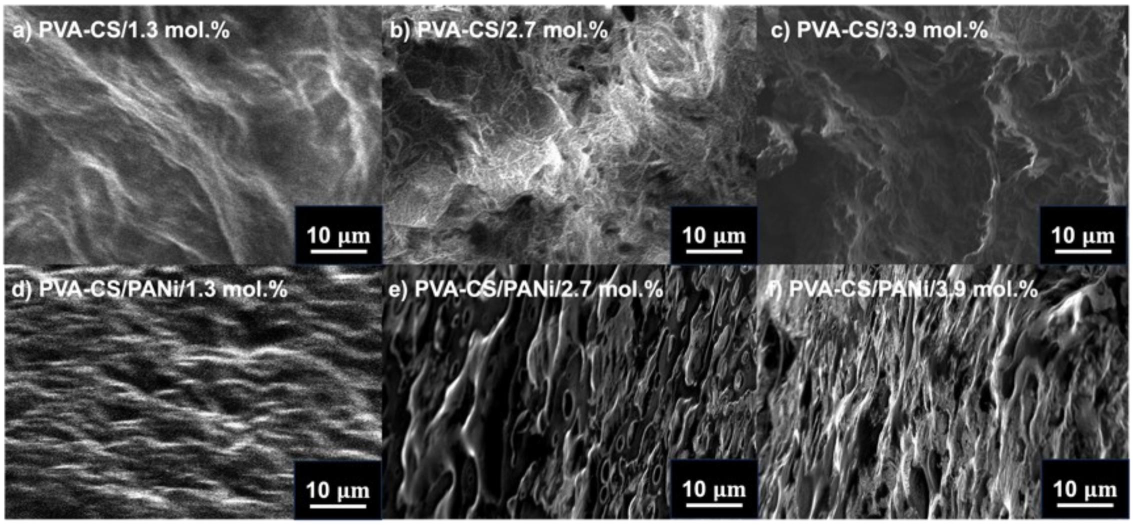

Figure 4. SEM images of PVA-CS hydrogel vs. PVA-CS/PANI with different PVA concentrations(a) PVA-CS hydrogel 1.3 mol.% (b) PVA-CS hydrogel 2.7 mol.% (c) PVA-CS hydrogel 3.9 mol.% (d) PVA-CS/PANi hydrogel 1.3 mol.% (e) PVA-CS/PANi hydrogel 2.7 mol.% (f) PVA-CS/PANi hydrogel 3.9 mol.%

3.6. Rheology Properties of PVA-Chitosan with Polyaniline

Dynamic rheological studies of gel samples were conducted to evaluate the PVA-CS/PANi hydrogels' mechanical properties with different concentrations of PVA. Each sample was tested in a rheometer at 1% constant strain and 1 Hz frequency corresponding to the linear viscoelastic range of the gel. G' and G" represent the elastic (storage modulus) and viscous (loss modulus) response, respectively. Based on Figure 5(a-b), it can be seen that the storage modulus was found to be larger than the loss modulus within a relatively smaller strain amplitude; this is an indicator that the rheological behavior in this region is dominated by an elastic, rather than a viscous property, which also indicates the reaction forming between polymer chains and crosslinkers as data shown in Table 2 and Table 3 [11]. Figure 5(a) shows the PVA-CS/PANi hydrogel with the increase of the storage modulus of reaction with the increased value of PVA concentrations (Table 2). The result demonstrates the ability of PVA-CS/PANi/3.9 mol.% hydrogel for SVG application as it shows the highest and greater value in both strain amplitude of 2356 Pa and frequency sweep of 3731 Pa. The increasing PVA concentration generally increases the viscosity and elastic modulus (storage modulus, G') of the hydrogel. This is because higher PVA concentrations result in a denser polymer network with more entanglements, which restricts the flow of the hydrogel and enhances its elastic behavior [12]. Moreover, when PANi is incorporated into hydrogels, its mechanical properties may be enhanced. Adding PANi into PVA-CS hydrogel can reinforce the hydrogel structure, leading to a higher elastic modulus and mechanical strength. PANi can act as physical cross-links within the hydrogel network, strengthening its overall structure [13].

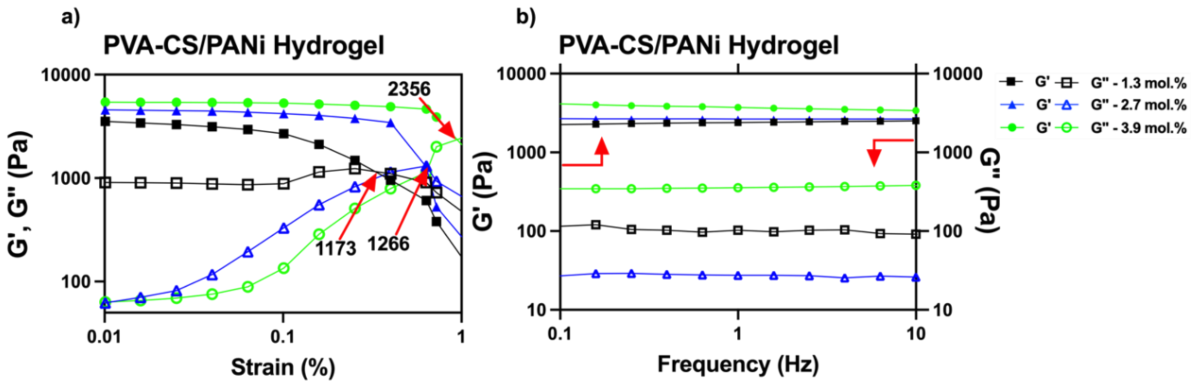

Figure 5. Rheology studies for PVA-CS/PANi with different concentrations of PVA (a) Strain amplitude of 1.3 mol.%, 2.7 mol.% and 3.9 mol.%; (b) Frequency-sweep of 1.3 mol.%, 2.7 mol.% and 3.9 mol.%

Table 2. Breaking point value of strain amplitude for PVA-CS/PANi with different PVA concentration

PVA concentration	Breaking point (Pa)
1.3 mol.%	1173
2.7 mol.%	1266
3.9 mol.%	2356

Table 3. Storage modulus and loss modulus value of frequency-sweep for PVA-CS/PANi with different PVA concentration

PVA concentration	Storage Modulus (G´) (Pa)	Loss Modulus (G´´) (Pa)
1.3 mol.%	2397.3	102.42
2.7 mol.%	2660	27.406
3.9 mol.%	3731	356.3

3.7. Swelling Test of PVA-CS/PANi hydrogel

Several factors influence a hydrogel's swelling capacity, including the concentration of the polymer used to form the hydrogel. As for PVA-CS hydrogels, the concentration of PVA can significantly affect their swelling behavior, as shown in Figure 6(a-d). Generally, as the PVA concentration increases, the hydrogel's swelling capacity decreases. This is because a larger PVA concentration increases the cross-links' density and results in a denser network structure, which restricts water uptake into the hydrogel. This explanation is supported by the research conducted by Ou et al., which states that a smaller concentration of PVA in the hydrogel resulted in a greater percentage of the degree of swelling hydrogel. In addition, the polymer chains in the hydrogel form physical crosslinks that impede the diffusion of water molecules, resulting in reduced swelling[14]. There's evidence shown in the equilibrium state of PVA-CS/PANi hydrogels with different PVA concentrations in Figure 6, where the water absorption of PVA-CS/PANi/1.3 mol.% was substantially higher compared to PVA-CS/PANi/3.9 mol.%. As a consequence of PANI's inherent hydrophobic nature, when incorporated into the PVA-CS hydrogel network, it can decrease the overall hydrophilicity of the hydrogel [15]. This hydrophobicity can impede the absorption of water by the hydrogel, resulting in a lower swelling capacity.

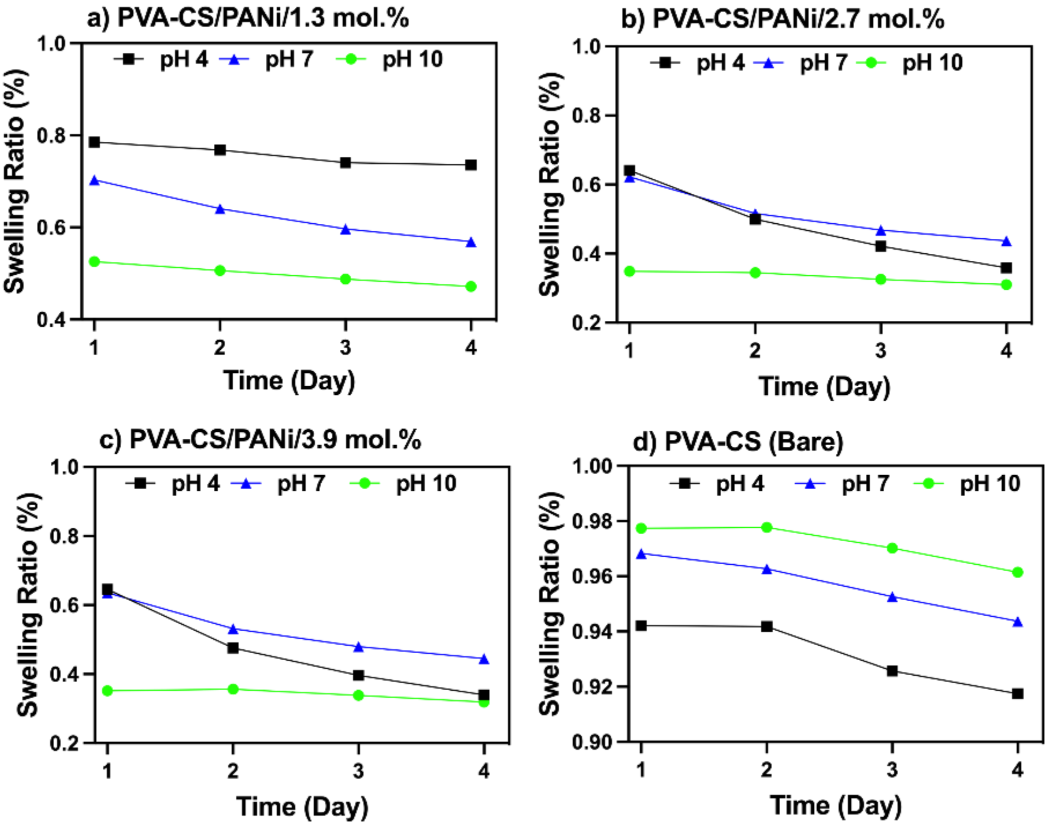

Figure 6. Swelling ratios of PVA-CS/PANi with different concentrations of PVA and PVA-CS hydrogel corresponding to pH (a) PVA-CS/PANi/1.3 mol.%; (b) PVA-CS/PANi/2.7 mol.%;(c) PVA-CS/PANi/3.9 mol.%;(d) bare PVA-CS

Figure 7 illustrates a noticeable difference between the PVA-CS hydrogel without PANi (Red) and the rest of PVA-CS/PANi hydrogel samples. PVA-based hydrogels' swelling behavior is often influenced by the pH of the medium [16]. A pH-sensitive hydrogels often exhibit significant changes in swelling or deswelling behavior in response to pH variations. This can be seen in Figure 7, which shows a different swelling capacity in PVA from low to high concentration; for instance, outside the optimal pH range, such as in highly alkaline conditions, the swelling capacity of the hydrogel can be significantly reduced. This phenomenon also explains the inconsistency between the morphology of these hydrogels (Figure 4) with swelling results (Figure 6), where the lowest PVA-CS/PANi inhibited the lower porosity but higher swelling absorption. However, the highest PVA-CS/PANi with greater porosity demonstrated the lowest swelling ability. Not only that, PANi as a conductive material may create an interaction between PVA-CS hydrogel with PANi in which when this hydrogel is immersed in acidic conditions, the presence of excess protons (H^+) leads to the protonation of PANi [17]. This protonation causes an increase in the hydrophilicity of the polymer, resulting in the absorption of water and subsequent swelling of the hydrogel (Figure 6(a)). The optimized PVA-CS/PANi hydrogel, despite its limited water absorption capacity, can still be leveraged effectively during the SVG process. By efficiently distributing the surface temperature of the hydrogel, it is possible to continuously and rapidly deliver water to the hydrogel's surface, thus enhancing its water intake and overall performance. This approach can be achieved by utilizing the hydrogel's dark property due to the incorporation of PANi.

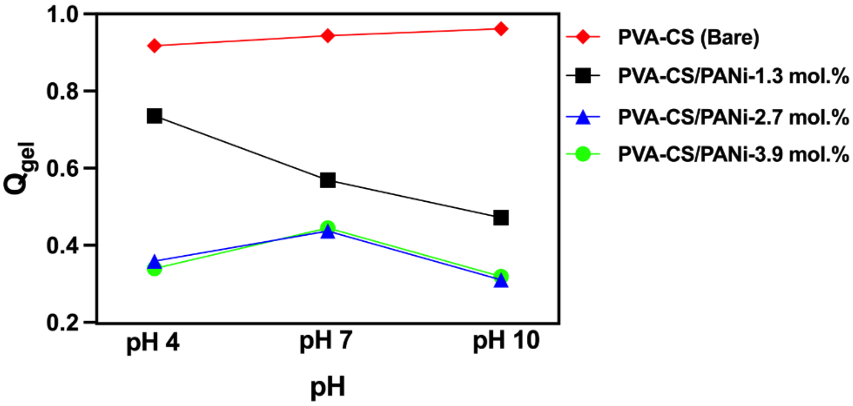

Figure 7. Equilibrium of PVA-CS/PANi with different concentrations of PVA and PVA-CS hydrogel corresponding to pH

Table 4. Equilibrium of PVA-CS/PANi with different concentrations of PVA and PVA-CS hydrogel corresponding to pH

Abbreviations	pH 4	pH 7	pH 10
PVA-CS/PANi 1.3 mol.%	0.73588	0.56908	0.47152
PVA-CS/PANi 2.7 mol.%	0.35884	0.43732	0.31012
PVA-CS/PANi 3.9 mol.%	0.33988	0.445	0.319
PVA-CS (Bare)	0.91744	0.94372	0.96148

3.8. UV-VIS Methylene Blue Absorption with PVA-CS Hydrogel

Methylene Blue (MB) is a commonly used dye in analytical chemistry, including water quality testing. It can be used to measure the presence of reducing agents or monitor a solution's oxidation-reduction potential [18]. In the case of clean water, where the concentration of reducing agents is typically low, MB can be used as an indicator to detect any reducing substances that may be present. The ultraviolet-visible spectrophotometry (UV-Vis) absorption spectrum of MB was used to monitor changes in its concentration or oxidation state when the PVA-CS hydrogel with different concentrations of PVA was immersed for 24 hours in MB dye solution. Typically, MB exhibits a characteristic absorption peak around 665 nm when measured using UV-Vis spectroscopy, as depicted in Figure 8. The highest absorption is denoted as MB Sol (before) (Red), which is the solution before immersion with hydrogels. This peak corresponds to the maximum absorbance wavelength for MB in its oxidized form [19]. The reducing substances were present in the water, where they can react with the MB and cause a decrease in its absorbance at 665 nm, as shown in Figure 8 for PVA-CS/1.3 mol.% (Black), PVA-CS/2.7 mol.%(Blue) and PVA-CS/3.9 mol.% (Green). The decrease in the extent of the absorbance indicates the concentration or reactivity of the reducing substances in the water. In this experiment, the highest reduction can be witnessed in PVA-CS/3.9 mol.% (Green) hydrogel is shown in the physical visibility of the gel. The influence of PVA concentration can contribute to the hydrogel's porous structure and surface area, allowing for greater dye adsorption. The hydrogel's porous network provides a greater surface area for the dye molecules to interact [20]. Other than that, the PVA-CS hydrogels may have chemical interactions with MB due to the hydroxyl groups in PVA that can form hydrogen bonds with the dye molecules. Additionally, the chitosan functional groups, such as amino groups, can have chemical reactions with the MB, such as dye-chitosan complexation or covalent bonding.

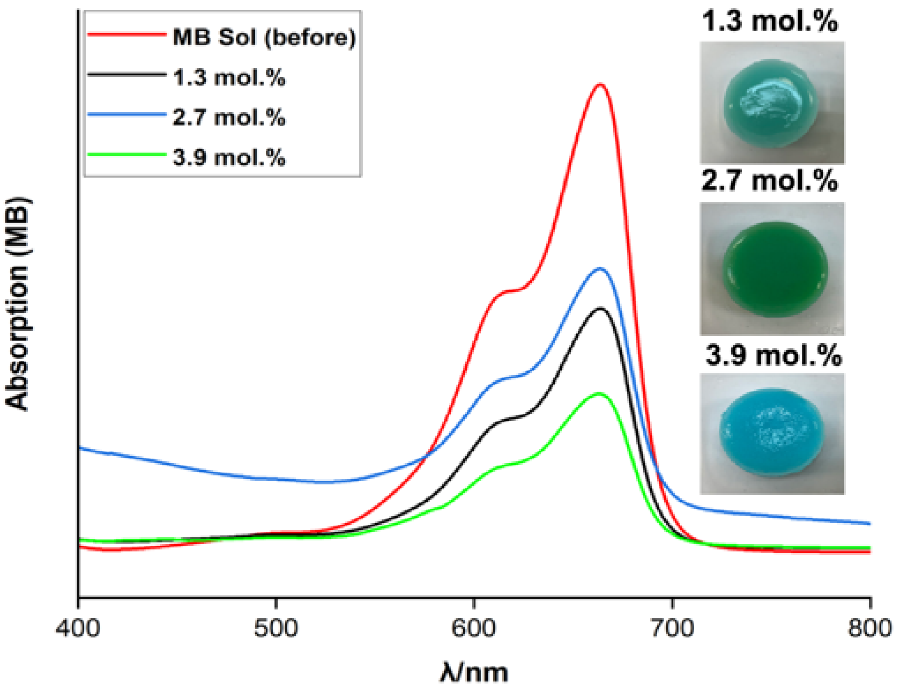

Figure 8. PVA-CS hydrogel UV-vis absorption of Methylene Blue (MB)

3.9. Solar Vapor Generation Efficiency

Enhancement of the SVG performance with hydrogel can be achieved by developing a dark hydrogel. A dark hydrogel absorbs more incident solar radiation, increasing heating and vapor generation. Also, selecting a polymer with a high absorption coefficient in the solar spectrum can be beneficial, such as PVA polymer, which allows for efficient light conversion into heat. Incorporating light-absorbing materials like PANi into the hydrogel formulation can enhance its absorption properties. PANi exhibits strong absorption in the visible and near-infrared regions of the solar spectrum. PANi can absorb a significant portion of the incident solar radiation when incorporated into PVA-CS hydrogel. This absorption is due to conjugated pi-electron systems within the PANi polymer backbone. Furthermore, upon absorption of solar radiation, PANi undergoes an electronic transition, generating excitons or charge carriers. These excitons or charge carriers undergo relaxation processes, during which they release excess energy as heat[21]. The heat generated within the PVA-CS/PANi raises the temperature of the surrounding environment, including the water within the hydrogel, increasing SVG efficiency (Figure 9). The absorbed heat from PVA-CS/PANi is transferred to the water present in the hydrogel, raising its temperature. As the water temperature increases, it can reach its boiling point, generating vapor. Based on the results in Figure 9, the PVA-CS/PANi shows greater efficiency than the PVA-CS hydrogel without incorporating PANi. The continuous water supply to the surface due to the porous structures of this hydrogel is proven, as previously discussed. Figure 10 shows the temperature distribution on the PVA-CS/PANi 3.9 mol.% surface increases due to the hydrogel's rich porosity and dark hydrogel's appearance. The PVA-CS hydrogel without PANi is physically white and causes reflection of the solar spectrum, making it less efficient when used alone for SVG. This observation may provide insight into how PANi influenced the performance to maximize the use of natural light incident and produce clean water. Moreover, as seen in Table 5, when compared to the earlier study conducted by Zhu and colleagues, the results showed a 4% improvement, which can be further enhanced through deliberate design in future studies [22].

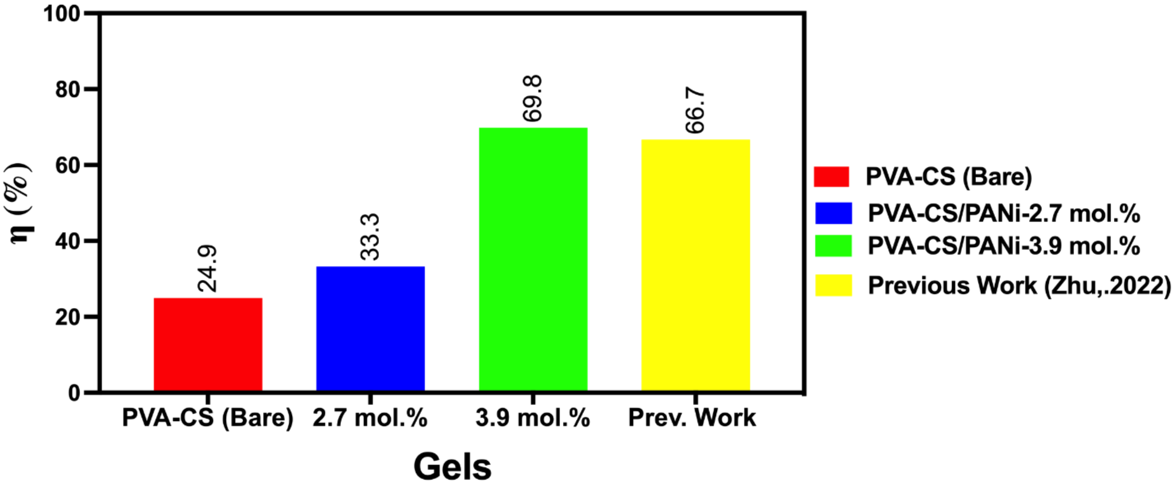

Figure 9. SVG efficiency of PVA-CS hydrogel and PVA-CS/PANi hydrogel

Table 5. The comparison of PVA-CS/PANi with previous work

Previous Work	**Zhu et al., 2022**	**This work**
Substrate	PVA-Chitosan	PVA-Chitosan
Light absorber	Carbon Nanoparticles (CNPs)	Polyaniline (PANi)
SVG Efficiency	66.7%	69.8%

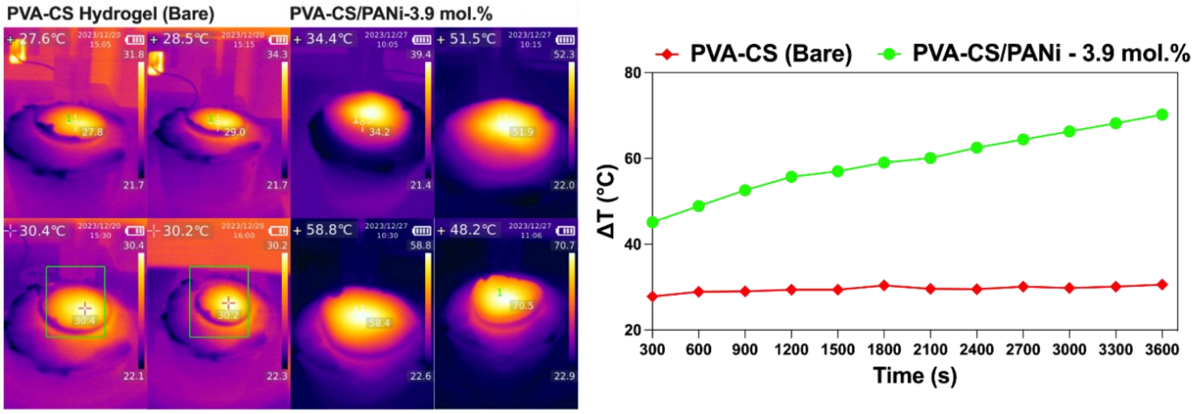

Figure 10. Water heating (ΔT- the temperature difference between the temperature before and after irradiation) was recorded in different illuminations over 1 hour period.

4. CONCLUSION

Based on the analysis of the results, the PVA-CS/PANi-3.9 mol.% hydrogel emerges as the most optimal choice. The findings highlight a significant improvement in the structure of the hydrogel's structure, the concentration of PVA concentration. The increase in concentration is essential to ensure a consistent water supply to the hydrogel's surface of the hydrogel during SVG. Furthermore, a higher hydrogel porosity signifies enhanced mechanical stability, as the increased storage modulus value observed in the rheology of PVA-CS/PANi 3.9 mol.%. The mechanical durability of the hydrogel is crucial for practical applications due to its continuous exposure to sunlight. Adding PANi to the PVA-CS hydrogel resulted in a darker appearance and higher light absorption capacity. This enhanced light absorption capability is also reflected in the temperature distribution on the surface of the hydrogel. As a result, the construction of SVG becomes more efficient, making it easier to generate clean water. The efficiency of PVA-CS/PANi 3.9 mol.% can be further improved by surface modification and optimizing the PANi concentration.

ACKNOWLEDGEMENT

This research was funded by UMP-IIUM-UiTM Sustainable Research Collaboration (SRCG) from Universiti Teknologi Mara and International Islamic University Malaysia, denoted as SRCG20-044-0044/ 100-TNCPI (1/1). The authors would also like to thank Majlis Amanah Rakyat (MARA) for their technical and financial support. The authors would like to acknowledge our collaborators, Dr. Wan Wardatul Amani Wan Salim, Dr. Nurul Sakinah Engliman, and Dr. Radhiyah Abd Aziz, for their invaluable input.

REFERENCES

[1] Schewe, J., et al., *Multimodel assessment of water scarcity under climate change.* Proceedings of the National Academy of Sciences, 2014. **111**(9): p. 3245-3250.

[2] Guo, Y., et al., *Synergistic energy nanoconfinement and water activation in hydrogels for efficient solar water desalination.* ACS nano, 2019. **13**(7): p. 7913-7919.

[3] Chen, C., Y. Kuang, and L. Hu, *Challenges and opportunities for solar evaporation.* Joule, 2019. **3**(3): p. 683-718.

[4] Bashir, S., et al., *Fundamental concepts of hydrogels: Synthesis, properties, and their applications.* Polymers, 2020. **12**(11): p. 2702.

[5] Khurma, J.R., D.R. Rohindra, and A.V. Nand, *Synthesis and properties of hydrogels based on chitosan and poly (vinyl alcohol) crosslinked by genipin.* Journal of Macromolecular Science, Part A: Pure and Applied Chemistry, 2006. **43**(4-5): p. 749-758.

[6] Khan, S. and N.M. Ranjha, *Effect of degree of cross-linking on swelling and on drug release of low viscous chitosan/poly (vinyl alcohol) hydrogels.* Polymer bulletin, 2014. **71**: p. 2133-2158.

[7] Yin, X., et al., *Macroporous double-network hydrogel for high-efficiency solar steam generation under 1 sun illumination.* ACS applied materials & interfaces, 2018. **10**(13): p. 10998-11007.

[8] Zhu, Z., et al., *Preparation and properties of high solid content and low viscosity waterborne polyurethane—Acrylate emulsion with a reactive emulsifier.* Polymers, 2018. **10**(2): p. 154.

[9] Chen, J., et al., *An adhesive hydrogel with "Load-Sharing" effect as tissue bandages for drug and cell delivery.* Advanced Materials, 2020. **32**(43): p. 2001628.

[10] Chen, Y.-N., et al., *Self-assembled polyvinyl alcohol–tannic acid hydrogels with diverse microstructures and good mechanical properties.* ACS omega, 2018. **3**(9): p. 11788-11795.

[11] Kakadjian, S., O. Rauseo, and F. Mejias. *Dynamic rheology as a method for quantify gel strength of water shutoff systems*. in *SPE International Conference on Oilfield Chemistry?* 1999. SPE.

[12] Kjøniksen, A.-L. and B. Nyström, *Effects of polymer concentration and cross-linking density on rheology of chemically cross-linked poly (vinyl alcohol) near the gelation threshold.* Macromolecules, 1996. **29**(15): p. 5215-5222.

[13] Han, J., T. Lei, and Q. Wu, *High-water-content mouldable polyvinyl alcohol-borax hydrogels reinforced by well-dispersed cellulose nanoparticles: Dynamic rheological properties and hydrogel formation mechanism.* Carbohydrate polymers, 2014. **102**: p. 306-316.

[14] El Sayed, M.M., *Production of polymer hydrogel composites and their applications.* Journal of Polymers and the Environment, 2023. **31**(7): p. 2855-2879.

[15] Nawaz, H., et al., *Hybrid PVDF/PANI membrane for removal of dyes from textile wastewater.* Advanced Engineering Materials, 2022. **24**(5): p. 2100719.

[16] Shivakumara, L.R. and T. Demappa, *Synthesis and swelling behavior of sodium alginate/poly (vinyl alcohol) hydrogels.* Turkish journal of pharmaceutical sciences, 2019. **16**(3): p. 252.

[17] Golba, S., et al., *Impact of acidity profile on nascent polyaniline in the modified rapid mixing process—Material electrical conductivity and morphological study.* Materials, 2020. **13**(22): p. 5108.

[18] Khan, I., et al., *Review on methylene blue: Its properties, uses, toxicity and photodegradation.* Water, 2022. **14**(2): p. 242.

[19] Fernandez-Perez, A. and G. Marban, *Visible light spectroscopic analysis of methylene blue in water; what comes after dimer?* ACS omega, 2020. **5**(46): p. 29801-29815.

[20] Ghafelebashi, A., et al., *A novel fabricated polyvinyl alcohol/bentonite nanocomposite hydrogel generated into colloidal gas aphron.* Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2022. **650**: p. 129580.

[21] Namsheer, K. and C.S. Rout, *Conducting polymers: a comprehensive review on recent advances in synthesis, properties and applications.* RSC advances, 2021. **11**(10): p. 5659-5697.

[22] Zhu, M., et al., *Dome-arrayed chitosan/PVA hydrogel-based solar evaporator for steam generation.* Scientific Reports, 2022. **12**(1): p. 4403.