



Effect of spent coffee grounds and rice husk amount towards the swelling properties of hydrogel using graft polymerization

S.S. Jamari, S.V. Vennu, S. Ghazali, S. Abd Rahim *

Faculty of Chemical and Process Engineering Technology, College of Engineering Technology, Universiti Malaysia Pahang, 26300 Gambang, Pahang, Malaysia

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ABSTRACT

Hydrogels are widely known for their ability to absorb water without being dissolved. This characteristic, which is known as swelling has been studied by many researchers in various sectors such as medicine, pharmacy, agriculture, health science and many more. This paper presents a study on the swelling properties of hydrogel that was grafted with spent coffee grounds and rice husk ash. The hydrogel was prepared with acrylic acid as the monomer and acrylamide as the co-monomer. The hydrogel was grafted with spent coffee grounds and rice husk ash separately, with varied weight percent (wt%). The hydrogel was characterized using Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM), Thermal Gravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC). The 0.1 (wt%) rice husk ash grafted hydrogel has the best swelling properties as shown by the highest water absorption, with the most porous structure and the highest crystalline temperature (122.0 °C). The FTIR wavenumber showed that the hydrogel is grafted properly as new wavenumbers are formed, whereas the TGA analysis shown that it had the highest decomposition temperature (658.6 °C).

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1. Introduction

Over the years, hydrogel has become a popular interest among researchers due to its promising wide range of applications. Moreover, studies have been carried out to develop better hydrogel properties in order to reduce the contamination of the inadequate biodegradability hydrogel to the environment [1]. Hydrogel is a network of polymer chains that absorbs water without dissolving. Due to this special characteristic, hydrogel has been used in many fields such as medicine, agriculture, pharmaceutical and many more [2].

The classification of hydrogel is based on its polymer origin; natural or synthetic [1,3]. Natural hydrogels are made of natural polymers such as collagen, which are biocompatible, biodegradable and also supports cellular activities but it has low mechanical strength and might contain biological pathogen. On the other hand, the synthetic hydrogel which are made from synthetic polymers has high mechanical strength and will not contain biological

pathogen. However, its biodegradability is quite low and toxic substances may present [1].

A study has been carried out by Rodrigues and co-workers in 2012 on the incorporated of rice husk ash to chitosan and (poly) acrylic acid as a superabsorbent hydrogel. The finding shows better swelling properties at different temperature due to high purity and crystallinity with the addition of rice husk ash. However, the hydrogel had a high pH sensitivity. The finding noted that the swelling of the hydrogel may also affected by a slight changes in pH [4]. Li and co-workers in 2016 evaluate the swelling properties of a wheat straw cellulose hydrogel that underwent a solution polymerization and graft copolymerization. It was learned that the hydrogel had a better swelling capacity in a neutral condition (pH 7). In addition, a larger size of hydrogel was also suggested to achieve a better controlled-release feature [5]. Sokker and co-workers in 2011 prepared a radiation induced graft polymerized hydrogel of chitosan based polyacrylamide for the adsorption of crude oil. The findings showed that hydrogel is very efficient for adsorbing crude oil but the drawback was polyacrylamide and its copolymers has shear degradability [6].

* Corresponding author.

E-mail address: syarifah@ump.edu.my (S. Abd Rahim).

It is notable that there are some drawbacks and there are rooms for improvement. There is a wide potential in the application of hydrogel, thus, the on-going study, looking for improvement towards the properties of the hydrogel such as better swelling and biodegradability suggested to be in place. In relation to the matter, the investigation on the swelling properties of hydrogel grafted with fillers is studied. The grafting substance (fillers) used were bio waste material i.e. rice husk ash (RHA) and spent coffee grounds (SCG) with the aims to utilize the bio waste materials in improvement of the swelling properties.

2. Materials and methods

2.1. Materials

The spent coffee grounds (SCG) and rice husk ash (RHA) used in this study were obtained from local coffee shop and rice factory. The sodium hydroxide (NaOH), nitrogen, acrylic acid (AA), acrylamide (AM), ammonium persulfate (APS), methylenebisacrylamide (MBA) and methanol were reagent grade supplied by Sigma Aldrich.

2.2. Hydrogel preparation

8.33 ml of AA and 4 ml of water were mixed and 8.33 ml of the mixture was taken out. 5 g of AM was mixed in the AA mixture. The solution was neutralised with a NaOH solution. The mixture was transferred into a 3-necked flask with a magnetic stirrer and was stirred for 5 min in room temperature at 300 rpm. During the stirring, 0.1 wt% (wt%) of rice husk ash and 0.01206 g of MBA were poured into the 3-necked flask. The temperature for the hotplate was set to 60 °C. Once the mixture reaches 60 °C, 0.804 g of APS was added into the mixture and a nitrogen pipeline was fixed to the 3-necked flask for purging the oxygen out of the system. The other 2 necks of the flask were closed using aluminium foil. The hydrogel was formed after 12 to 15 min of stirring at 300 rpm. The procedure was repeated for 0.2 wt%, 0.3 wt%, 0.4 wt% and 0.5 wt% of rice husk ash. The hydrogel produced was soaked in methanol for 20 min and being washed using distilled water to remove all the suspended particles, followed by placed it in the oven at 60 °C for 3–4 days until it's totally dry. The procedures started earlier were repeated for the second filler i.e spent coffee grounds [7].

2.3. Water absorbency analysis

3 g of hydrogel was placed in a teabag and was immersed in distilled water. The weight of the hydrogel was checked every 15 min until the weight becomes constant. Prior to weighing the teabag filled with hydrogel, the teabag was pat on a tissue paper to remove the water on the surface of the teabag. The absorbency was calculated according to Equation (1):

$$\text{Absorbency} = \frac{M - M_0}{M_0} \quad (1)$$

The M and M_0 is mass of swollen and dry hydrogel respectively [4].

2.4. Hydrogel characterization

The functional group of the grafted hydrogel was analysed using a Fourier Transform Infrared Spectroscopy (FTIR). The hydrogel was blended to make it as a powder form prior to the analysis [8]. The morphology of the hydrogel was observed using a Scanning Electron Microscope (SEM). Prior to the measurement, the

hydrogel was coated with gold [9]. A Thermal Gravimetric Analysis (TGA) system was used to study the proportion of the grafted spent coffee grounds and rice husk chain in the hydrogel. The sample was heated from 35 °C to 900 °C [10]. Finally, the melting point was obtained using a Differential Scanning Calorimetry (DSC) at 10 °C/min from 40 °C to 300 °C [6].

3. Results and discussion

3.1. Water absorbency analysis

Water absorbency of hydrogel was calculated using an initial weight of 1 g of dried hydrogel. The hydrogel was left to soak overnight in distilled water and the final reading was taken. Fig. 1 shows the water absorbency of hydrogel at different weight percent of rice husk ash (RHA) and spent coffee grounds (SCG).

Fig. 1 shows that for both the fillers, the absorbency decreases with increasing weight percent of fillers. This can be due to the increase of crosslinking points in the polymer chain that is caused by the chemical and physical interaction of the rice husk ash with the polymer matrix that results in a decrease in elasticity [10].

There is a constant trend of decrease in the absorbency with the increase of the weight percent (wt%) of RHA. 0.3 wt% and 0.4 wt% has somewhat about the same value of absorbency. A sharp decrease is noted from 0.1 wt% to 0.2 wt%. As for the spent coffee grounds grafted hydrogel, the absorbency decreases slowly until 0.3 wt% and then has a sharp decrease from 0.3 wt% to 0.5 wt%. This is because spent coffee ground is a material with very low porosity and therefore, after 0.3 wt%, the hydrogel becomes too concentrated with an increase of crosslinking points.

The comparison with the controlled hydrogel shows that it has an absorbency of 100.75 g/g and the 0.1 wt% of RHA and 0.1 wt% of SCG is slightly higher (105.47 g/g and 102.39 g/g, respectively). This swelling property can also be related to the hydrophilicity of the hydrogel with water [6].

3.2. Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR analysis was used to observe the functional group of hydrogel. The peaks obtained with the controlled hydrogel were compared with the grafted hydrogel to observe the grafting of RHA and SCG. The FTIR analysis of 0.1 wt% of RHA grafted hydrogel shows many peaks were shifted and some new peaks were present as compared to the controlled hydrogel possibly due to the grafting process. The peak at 1060 cm^{-1} and 794 cm^{-1} in RHA that represents the O-Si-O symmetrical and asymmetrical stretching respectively are not present in the grafted hydrogel [11,12]. This may suggest that the RHA is properly grafted into the hydrogel.

The comparisons with the controlled hydrogel FTIR analysis, a few new peaks are formed after the grafting. The peak at

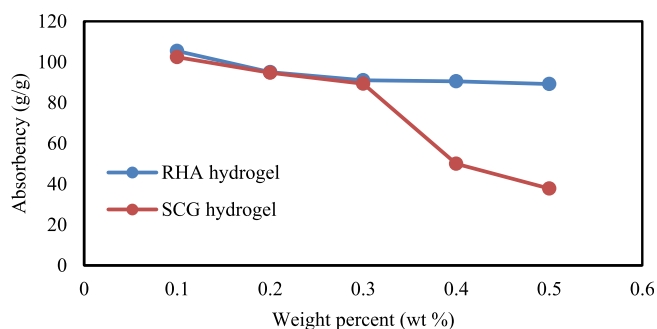


Fig. 1. Water absorbency of RHA and SCG grafted hydrogel.

1700 cm^{-1} can be attributed to the C=O of the acid functional group and the peak at 1119 cm^{-1} is linked to the C-O-C stretch [13]. These peak is not found at the controlled hydrogel. Moreover, it can be suggested that the broad band from 3500 cm^{-1} to 3200 cm^{-1} possibly related to the hydrogen bonded water as there is still some moisture left in the hydrogel [14].

The FTIR analysis of 0.1 wt% of SCG grafted hydrogel shows that the peak of 2920 cm^{-1} in the SCG analysis attributes to the C-H stretch [15] is not present in the grafted hydrogel. The peak in between 3000 cm^{-1} to 3600 cm^{-1} which representing the stretching of O-H and N-H bond of SCG also not present in the grafted hydrogel [12]. The new peak at 1133 cm^{-1} and 1313 cm^{-1} represent the secondary amine C-N stretch and an aromatic amine tertiary C-N stretch respectively were seen in the analysis [12] suggested the possibility of SCG is grafted properly into the hydrogel.

3.3. Differential Scanning Calorimetry (DSC)

The DSC analysis of the controlled hydrogel shows a sharp endothermic peak occurred at $40\text{ }^{\circ}\text{C}$ which is also representing the melting temperature (T_m). Two more broad endothermic peaks were observed at $135\text{ }^{\circ}\text{C}$ and $278\text{ }^{\circ}\text{C}$. Three exothermic peaks are observed at $101\text{ }^{\circ}\text{C}$, $213\text{ }^{\circ}\text{C}$ and $247\text{ }^{\circ}\text{C}$. The small exothermic peak suggest that the hydrogel became amorphous instead of crystalline. In the DSC thermogram of the RHA, its crystalline temperature (T_c) is at $550\text{ }^{\circ}\text{C}$ [16]. In comparison to the 0.1 wt% RHA grafted hydrogel, two broad endothermic peaks are at $211\text{ }^{\circ}\text{C}$ and $279\text{ }^{\circ}\text{C}$. It also has a sharp endothermic peak at $40\text{ }^{\circ}\text{C}$ suggesting it to be T_m . There is a sharp exothermic peak at $122\text{ }^{\circ}\text{C}$ and there is a broad exothermic peak at $243\text{ }^{\circ}\text{C}$. This suggest that the crystalline temperature (T_c) is at $122\text{ }^{\circ}\text{C}$. These peaks are totally different with the controlled hydrogel and RHA peaks suggesting that

after grafting, a new thermal property is formed by the hydrogel. However, the melting point still remains the same.

The 0.1 wt% SCG grafted hydrogel was analysed alongside the DSC thermograms of SCG and controlled hydrogel. In the analysis of SCG, it was learned that the T_m was at $76.89\text{ }^{\circ}\text{C}$ and its thermal depolarization and branching of SCG happened at a temperature range of $220\text{ }^{\circ}\text{C}$ to $310\text{ }^{\circ}\text{C}$ [17]. The DSC analysis of the SCG grafted hydrogel shows there are two broad endothermic peaks at $203\text{ }^{\circ}\text{C}$ and $285\text{ }^{\circ}\text{C}$ and two exothermic peaks at $103\text{ }^{\circ}\text{C}$ and $231\text{ }^{\circ}\text{C}$. The T_c is at $103\text{ }^{\circ}\text{C}$ because of its sharper peak. It can be seen that the melting point of all 3 hydrogels are the same but the crystallization temperature varies. Therefore, this grafted hydrogel has retained certain peaks and also produced new peaks causing its thermal property to differ from the controlled hydrogel, RHA and SCG. T_m is usually different for different types of hydrogel due to the type of polymerization and also the materials used. The exothermic peak is used to show the crystalline structure of the hydrogel. After $300\text{ }^{\circ}\text{C}$, all the materials in the hydrogel are decomposed [18].

3.4. Scanning Electron Microscope (SEM)

The SEM analysis was used to observe the morphology of the hydrogel and is shown in Fig. 2. Through the micrographs, the 0.1 wt% RHA grafted hydrogel has the densest morphology and it has many pores that is able to absorb water.

This dense morphology with many pores were suggested to be the possible reason resulted the 0.1% RHA grafted hydrogel has a higher water absorbency rate as compared to the others. It can also be noted that 0.1 wt% SCG and RHA grafted hydrogel seem to be alike to a thin sheet of material [17]. This compliments with the swelling test as 0.1 wt% of RHA grafted hydrogel had the highest swelling rate as compared to the controlled hydrogel, 0.1 wt% RHA grafted hydrogel is evidently more porous. This suggested that as the RHA hydrogel crosslinked by MBA, it forms strong grid walls,

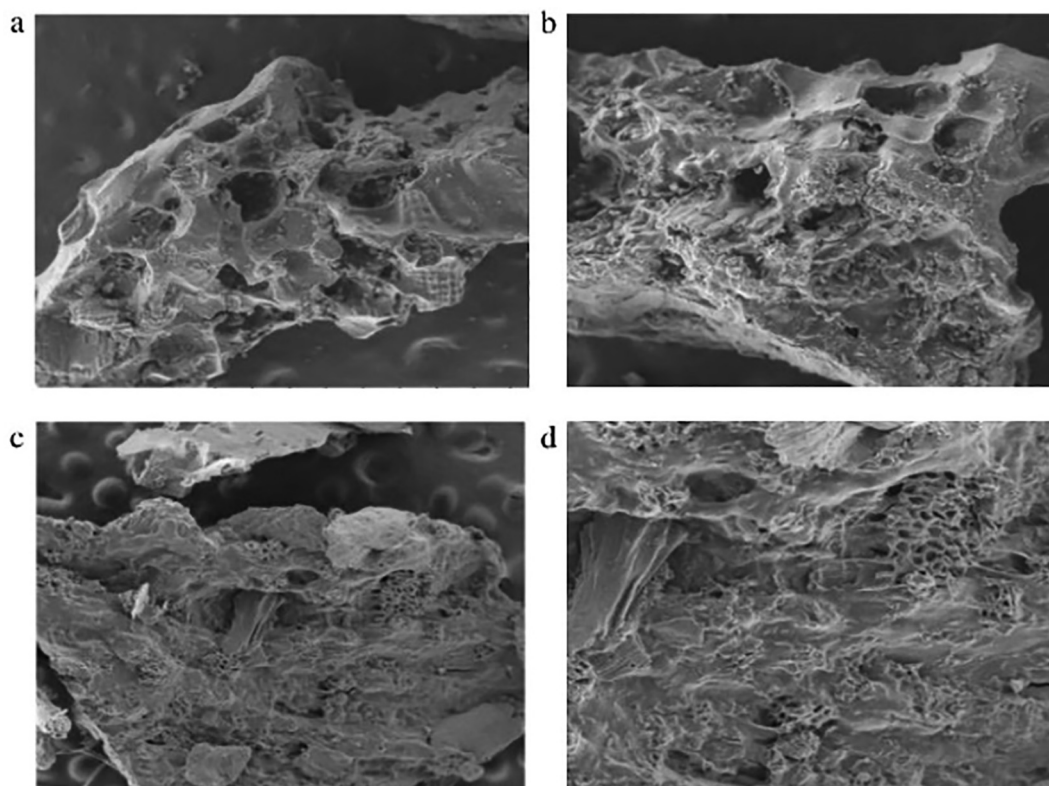


Fig. 2. SEM images of (a) $50\times$ (b) $100\times$ 0.1 wt% RHA hydrogel, (c) $50\times$ (d) $100\times$ 0.1 wt% SCG hydrogel.

thus, more proportion of water can be held in the grids [10]. The pore size in the analysis does not reflect the magnitude of water diffusion in the swollen state as the hydrogel is at a dry condition.

3.5. Thermal Gravimetric analysis (TGA)

The TGA analysis was carried out on the controlled sample, 0.1 wt% RHA grafted hydrogel and 0.1 wt% SCG grafted hydrogel. Three distinct zones were observed in the analysis of the controlled hydrogel. The initial decomposition temperature, T_{id} is at 188.24 °C. The temperature at maximum rate of weight loss, T_{max} is 388.20 °C and the final decomposition temperature, T_{fd} is 654.03 °C. The residue was left with 5.182%.

The 0.1 wt% RHA grafted hydrogel, has the initial decomposition temperature, T_{id} of 66.34 °C, temperature of maximum rate of weight loss, T_{max} at 399.10 °C and the final decomposition temperature, T_{fd} of 658.56 °C with the final residue at 19.33%. The 0.1 wt% RHA grafted hydrogel has a higher T_{max} and T_{fd} than the controlled hydrogel but the T_{id} is significantly lower. This might be due to the presence of water in the hydrogel that evaporated [19]. The high value of T_{max} and T_{fd} might be due to the properties of rice husk ash itself that has a high T_{max} value of 360 °C. The degradation at T_{max} might also be due to the thermal decomposition of cellulose and hemicellulose in RHA [20].

On the other hand, for the 0.1 wt% of SCG grafted hydrogel, the initial decomposition temperature, T_{id} is at 63.95 °C, temperature at maximum rate of weight loss, T_{max} is at 437.61 °C and the final decomposition temperature, T_{fd} is at 643.51 °C with a final residue of 9.847%. Similar to previous hydrogel, this SCG grafted hydrogel has a much lower T_{id} temperature due to the evaporation of the excess water in the hydrogel [19]. The T_{max} is higher than RHA grafted hydrogel and controlled hydrogel. This possibly due to the depolymerisation and decomposition of polysaccharides in the hydrogel [17].

4. Conclusion

In this study, it can be concluded that 0.1 wt% of RHA grafted hydrogel showed the highest water absorption (105.47 g/g). The FTIR analysis shows all of the hydrogel were properly grafted as some of the functional groups of RHA and SCG were no longer found in the grafted hydrogel. The new peaks originally are not found in the controlled hydrogel and also in SCG and RHA were formed. The melting point of this grafted hydrogel remained the same as the controlled hydrogel which is at 40 °C but the crystalline temperature of the grafted hydrogel changed to 122 °C and 103 °C for RHA and SCG respectively. The SEM analysis suggested that the 0.1 wt% RHA hydrogel is the most porous. The TGA and DSC analysis suggest that the RHA grafted hydrogel can withstand higher temperature than the SCG grafted hydrogel. Thus, the findings suggested that the 0.1 wt% RHA grafted hydrogel has the best swelling properties.

CRedit authorship contribution statement

S.S. Jamari: Methodology. **S.V. Vennu:** Data curation, Writing - original draft. **S. Ghazali:** Conceptualization, Writing - review editing. **S. Abd Rahim:** Supervision, Writing - review editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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