Investigation on the water absorbency, chemical and thermal properties of superabsorbent poly (acrylic acid-co-acrylamide)/spent coffee ground composite

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Abstract. Superabsorbent polymer (SAP) is defined as a material that can absorb huge amount of water while remain its original shape without loss the water or aqueous solution that had been absorb. The incorporation of filler in SAP could increase the water absorbency of the polymer. Thus, this work aim to investigate the properties of spent coffee ground (SCG) bio-filler into the SAP network using inverse suspension polymerization method. The structural, thermal and also morphological characterizations of the synthesized SAPs were performed by FTIR, TGA, and FESEM techniques. Based on the results obtained, the optimum of water absorbency of SAP was shown at SAP_0.05SCG filler respectively. For the effect of filler loading, the observed result was supported by FESEM microstructures of SAP where the surface morphology of all sample with varied filler composition shown coarse surface. It is observed using FTIR spectra that the O-H band is broader and sharper at SAP_0.05SCG compared to the control and the SCG filler. For the TGA, the SAP_0.05SCG is easier to thermally degrade compared to the control. Thus, this research has proved that the SCG is able to enhance the water absorbency of superabsorbent polymer which could give better contributions in various applications.

1. Introduction

Superabsorbent polymers (SAPs) are complex hydrophilic polymers, which are chemically or physically highly cross-linked, possess with the ability of absorbing and retaining large amounts of water and other liquids [1]. SAPs also is capable to maintain its physical structure and having stable polymer network even in its swollen state thus an advantage properties over conventional water-absorbing materials [2]. Acrylic and acrylamide monomers are the most common raw materials for the SAPs production. These monomers are fully synthetic based materials which has poor degradation rate, indirectly becoming an environmental concern [1,3]. As the trends have been paving the path towards the eco-friendly and partial synthetic SAPs composite [4], additional of bio-filler, such as cellulose, starch and spent coffee ground, is a sustainable options.

Recently, interests on the bio-filler addition in the SAPs polymer networks have attracted much attention [1,4,5]. Addition of bio-filler in the SAPs composite can improve the water absorbency and retention, biodegradability rate as well as environmental capability of the SAPs composite. Spent coffee ground (SCG), is a bio-filler, in which main residue of the brewing process [6], and insoluble remainder that left after coffee beans are dehydrated, milled and brewed. Besides, SCG has hydrophilic characteristic that is suitable as bio-filler to the SAPs [7]. Currently, SCG is used as the fertilizer for small plants; however, the increasing amount of SCG produce yearly has caught the
attention of researchers. Recently, the SCG is used as raw materials or support for different applications, such as filler for composite [7], adsorbents [8], energy [6] and construction material [9]. Apparently, there is still no work reported on the application of bio-filler SCG in SAPs composite using inverse-suspension polymerization. Inverse suspension polymerization is one of a polymerization technique in which water-soluble monomer is dispersed in a continuous organic matrix. This polymerization technique, in generally, produce bead shapes SAPs with size range of between 1µm to 1 mm [10], thus the products can directly be applied.

The main objective of this research is to investigate the effect of SCG bio-filler addition into the SAP network for Poly(acrylic acid-co-acrylamide)/SCG composite production. Accordingly, the quantities of SCG to synthesize the SAP of Poly (acrylic acid-co-acrylamide)/SCG are manipulated to observe the water absorption capability. The structural, thermal and also morphological characterizations of the synthesized SAPs were performed by FTIR, TGA, and SEM techniques.

2. Experimental

2.1. Materials
The spent coffee ground is the residual materials that obtained the local kopitiam shop. Chemicals used in this experiment were acrylic acid (AA) with 99% purity, acrylamide (AM) for synthesis grade, N,N’-Methylenebis(acrylamide) (NNMBA) with 99% purity, ammonium persulfate (APS) with 98% purity, sorbitane anhydride monostearic acid ester (Span-80), cyclohexane with 99.5% purity and sodium hydroxide for analysis grade. All the chemicals were supplied by Merck.

2.2. Methods
Synthesis of SAP_SCG via Inverse Suspension Polymerization. The continuous phase was prepared by mixing cyclohexane, span-80, cross-linker (NNMBA) solution and SCG (0-0.05 wt%) in a flask. The mixture solution was heated to 60°C with nitrogen purged for 15 minutes. After that, the dispersed phase was prepared by partially neutralized acrylic acid, acrylamide and initiator (APS) solution. The dispersed phase was then added slowly into the flask and the reaction held for 3h at 60 °C with 300 rpm agitation speed. The SAP_SCG beads were filtered, washed and dried in the oven at 60 °C until constant weight [11].

2.2.1 Water Absorbency Measurement. 0.01g of SAP_SCG is placed into a tea bag and then the bag is immersed in the beaker with distilled water until equilibrium/constant weight. The tea bag is allowed to drain for 10 minutes until excess water is removed and then been weighed. Water absorbency, \( Q \) (g water/g dry sample), is calculated by using the following equation 3.1:

\[
Q = \frac{m_2 - m_1}{m_1}
\]

where \( m_2 \) is the weight of sample after immersed and \( m_1 \) is the weight of sample before immersed in distilled water.

2.2.2. Characterization. The bio-filler and SAPs composite were characterized by iS50 Thermo scientific Fourier Transformed Infrared Spectroscopy (FTIR) with DTGS detector. The bands were recorded within the region from 4000 to 500 cm\(^{-1}\) to determine the surface functional groups. The surface morphology was analyzed using EVO 50 (ZEISS, USA), Field Emission Scanning Electron Microscopy (FESEM). The samples were fully coated with platinum by a sputter coater before the FESEM analysis. While the thermal properties will be characterized using TA instrument TGA Q500 between 25 °C to 800 °C at a heating rate of 10 °C/min under nitrogen gas flow.
3. Result and Discussion

3.1. Water absorbency
The quantification of maximum water uptake when the superabsorbent polymer is immersed in the excess water can be achieved through the water absorbency experiment. Figure 1 shows the water absorbency data of the SAPs at different SCG content using distilled water. The water absorbency of the SAP_SCG increased proportionally with the increasing of the bio-filler content. It can be observed that the water absorbency attained its maximum amount; 270 g H₂O/g absorbent, when the SCG content is at 0.05 wt%. While, the lowest water absorbency value is at control sample (0 wt% SCG) with value of 140 g H₂O/g absorbent.

This proves that spent coffee ground filler gives direct effect in enhancing the absorption of water in this polymer. SCG is mainly comprised of fibres existing as lignocellulose associated compounds, and acid detergent fiber which is composing of cellulose and lignin [7]. The presence of the lignocellulosic compound indirectly increases the hydrophilic characteristic of SAP_SCG that exhibits ionic group that helps SAP bonding with water molecule. Besides, SCG has higher water holding capacity compared to other materials such as rice husk and wheat straw, which could related to the increment of water absorbent capability in SAP_SCG [12].

![Figure 1. Water Absorbency of Poly (AA-co-AM)/SCG at different SCG content.](image)

3.2. Functional groups analysis
The functional groups of SCG bio-filler, control SAP, SAP_0.01SCG and SAP_0.05SCG were determine through the FTIR analysis. Generally, the pattern of the FTIR spectra for all the samples is relatively similar while the transmittance peaks is sharper with the addition of SCG filler in the SAP. Besides, major differences can be seen in the O-H absorption bands between 3600-3250 cm⁻¹. The hydroxyl stretching corresponds to the hydroxyl bonds of water [13], and it is observed that the O-H band is broader and sharper at SAP_0.05SCG compared to the control and the SCG filler. This also reflects with the water absorption capacity of SAP filled with SCG bio-filler (Figure 1).

Additionally, the C-H stretching vibration peaks also appeared in each sample of the control SAP, SAP_0.01SCG and SAP_0.05SCG with varying intensity and shifting peaks in the range of 2938-2292 cm⁻¹. This is due to the poly (acrylic acid) chains that were grafted onto the bio-filler during the polymerization process. Similar behavior is also detected for the carbonyl stretching of the conjugated carboxylic acid groups between wavenumber 1701.39 to 1563.09 cm⁻¹. The presence of C-N absorption band is recorded between wavenumber of 1100 to 1120 cm⁻¹ for control, SAP_0.01SCG
and SAP_0.05SCG. This indicates the C-N stretching of aliphatic amines group in the polymer matrix due to the cross linker agent addition during the inverse suspension polymerization [14].

**Figure 2.** Infrared Spectra of bio-filler (SCG), Control (SAP without SCG), SAP_0.01SCG and SAP_0.05SCG.

3.3 Thermal behavior analysis

Thermogravimetric analysis is an accurate method for investigating the decomposition pattern and thermal stability of polymers over a wide range of temperature. Figure 3 shows the thermogravimetric curves for SCG filler, control SAP and SAP_0.05SCG to determine effect of filler loading towards the thermal stability. In general, the SAP_0.05SCG is easier to degrade compared to the control SAP. Both elements show significant difference in weight loss below 200 °C, implying loss of moisture. It recorded between 31 to 34% compared to the 12% of weight loss for the SCG filler.

**Figure 3.** TG curve of bio-filler (SCG), Control (SAP without SCG), SAP_0.05SCG.

It can be observed from Figure 3 that the degradation of SCG filler is occur between 280 °C and 500 °C, whereas the degradation of SAP component is occur between 250 °C and 900 °C. The SCG filler is an organic material, which expected to contain lignocellulosic materials; hemicellulose, cellulose and lignin [15]. As nearly 40 wt% of SCG filler thermally decompose between temperatures of 280 to 500 °C, indicating most of the component in the SCG filler is cellulose. While, the SAP is an inorganic material consist of single and double bonds polymer structure which stabilize the thermal degradation. The thermal decomposition process of SAP_0.05SCG starts at a higher temperature; 320 °C, compared to the control SAP and SCG. Besides, the weight loss of samples decreased rapidly
implying a loss of moisture, dehydration of saccharide rings and breaking of C=O saturated aliphatic bonds in the main chain[16]. Thus, indicating that addition of filler in the polymer matrix is having thermally stable in low temperature, however, rapidly decompose at higher temperature.

3.4. Surface morphology
The surface morphology of the control SAP and SAP_SCG were investigated through FESEM analysis shown in Figures 4 and 5. Figure 4 shows the morphology of control SAP at two different magnifications (500 and 5000 X). Beads shape can be observed clearly for the control SAP at 500 X magnification, indicating that complete inverse suspension polymerization occurred[17]. However, the addition of bio-filler prevent the beads formation in the polymer due as the polymer materials (acrylic acid (AA), acrylamide (AM) are clumped together with spent coffee ground filler which as reduce the potential for bead formation during the inverse suspension polymerization.

![Figure 4. Surface Morphology of SAP as control at Magnification (a) 500 X and (b) 5000 X.](image)

![Figure 5. Surface Morphology of (a) SAP_0.1SCG, (b) SAP_0.5SCG at 500 X Magnification.](image)

The surface morphology of control SAP is smooth and dense due to the polymerization and non-filler addition, as illustrated in Figure 3(b). However, coarse surface morphologies are recorded for the SAP_0.01SCG and SAP_0.05SCG in Figure 5. The addition of SCG as filler offer major morphological changes on the surface of the composite compared to the control, which can be predicted to increase the surface area of the composite hence increase the water absorbency.

4. Conclusion
As a conclusion, SCG bio-filler has been successfully incorporated with the superabsorbent polymer via inverse suspension polymerization. The water absorbency trend increase with the addition of the SCG filler, with SAP_0.05SCG recorded the highest value; 270 g/g. The observed result was supported by FESEM microstructures of SAP_SCG where the surface morphology of all sample with varied filler composition shown coarse surface. While, the effect of chemical properties observed using FTIR spectra that the O-H band is broader and sharper at SAP_0.05SCG compared to the control and the SCG filler, indicating higher water absorbency capacity of the composite. In term of thermal stability, the SAP_0.05SCG is relatively stable at lower temperature (< 300 °C) however; rapidly decompose at higher temperature, which is more appropriate for daily usage application. Based
on the properties, the SAP_SCG has excellent water absorbency, which proved that it was suitable for agriculture and horticulture prospects.

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