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SYNTHESIS OF SUPERABSORBENT CARBONACEOUS KENAF COMPOSITE USING GRAFT POLYMERIZATION TECHNIQUES

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ABSTRACT

Carbonaceous fiber produced via Hydrothermal Carbonization (HTC) process of Kenaf fiber was used as the filler for superabsorbent carbonaceous composite (SPC). The SPC were applied as water adsorbents in agriculture field to increase soil absorption and water holding capacity.These characteristic are very essential to experience the effect of dehydration and minimize the effect of drought stress in crops. This work aimed to synthesize the superabsorbent carbonaceous kenaf fibers at different amount of carbon filler. The SPC were synthesized by graft polymerization using carbonaceous fibers with sodium hydroxide (NaOH), acrylic acid (AA), N,N'-methylene bisacrylamide (MBA) as cross-linker and also ammonium persulfate (APS) as initiator. Tea bag method was used to measure the equilibrium swelling ratio in deionized water of the synthesized SPC. The structure and morphologies of the SPC were characterized by Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscope (SEM). Overall results show that the water absorbency increased from 166.25 to 237.15 g water/g sample with the increasing of carbon filler from 0.1 to 0.5wt%. In conclusion, low cost superabsorbent material can help to retain nutrients by adding carbonaceous fiber content and absorb water in soil with various applications for plant growth and soil condition which will be useful especially in agriculture field.

Keywords: hydrothermal carbonization process, kenaf fiber, superabsorbent, carbonaceous fiber.

INTRODUCTION

Malaysia is honoured with tropical and damp atmosphere all through the whole year which is an advantage for farming area (Mekhilef *et al.* 2011). Therefore, agriculture sector give profitability in Malaysian economy. Maintaining a sustainable of high quality of soil and organic fertilizer will help to boost the profitability of farming system. Thus, well managed soils by addition of organic matter such as biomass into fertilizer can result in reduce costs and intend to less risk of erosion and run-off.

Kenaf has been introduced as a potential non-wood fiber in Malaysia under 9th Malaysian plan 2006-2010 (Mosello *et al.* 2010). The scientific name of Kenaf which is Hibiscus cannabinus L. (Chen *et al.* 2013), (Anfinrud *et al.* 2013), (Falasca *et al.* 2014), (Paridah *et al.* 2014), (Tigka *et al.* 2013), (Zhang *et al.* 2011) is one of the raw materials with environmental friendly and most economically essential harvests in non-wood fiber production (Zhang *et al.* 2011). It is fast growing plant and in almost four month can be ready for harvesting. This is the reason of Kenaf is suitable for tropical and sub-tropical which is warm temperature areas (Falasca *et al.* 2014). As a herbaceous plant it can produce high content of cellulose in average of 44 to 63.5% and hemicellulose in average between 15 and 23% (Zainuddin *et al.* 2013). Kenaf is commercialise used as paper production (Falasca *et al.* 2014), polymer reinforcement (Azwa and Yousif, 2013), bedding material of horses, cattle, poultry and rodents (Lips *et al.* 2009) and others.

A conversion process of natural fibrous material into carbonaceous fiber (hydrochar) is known as the hydrothermal carbonization process (HTC) (Lu *et al.* 2014), (Inoue, 2010). HTC is a favourable way to convert or transfer lignocellulosic biomass to value-added products and save energy through thermochemical process (Inoue, 2010), (Jamari and Howse, 2012), (Xiao *et al.* 2012). In addition, hydrochar presents the primary result of HTC process. Besides, hydrochar can be described as high carbon content, increased homogeneity, efficient grind ability and hydrophobic behaviour compared to its raw material. The potential applications of hydrochar are soil fertilizer, catalyst, energy storage or absorbent (Sermyagina *et al.* 2015). HTC is a convenient process which is faster and easier compared to natural process (Kambo and Dutta, 2014), (Titirici *et al.* 2007), (Parshetti *et al.* 2013).

Superabsorbent Polymer (SAP) product has hydrophilic structure of which renders them capable for holding a lot of water (Lanthong, Nuisin and Kiatkamjornwong, 2006), (Liang, Liu and Wu, 2007) saline water or any types of liquids up to hundreds of times their particular weight which constitute a group of polymeric materials (Rashidzadeh and Olad, 2014), (Casquilho *et al.* 2013), (Balbir Singh Kaith, 2010), (Dafader, 2009), (J. Akhter, 2004), (Zohuriaan-mehr and Kabiri, 2008). SAP also comparable materials to natural tissues due to their ability can hold a large amount of water (Zohuriaan-mehr and Kabiri, 2008). The existent of ionic functional groups in SAP resulted the ability to absorb a lot capacity of water (Balbir Singh Kaith, 2010). SAP has discovered potential applications in numerous fields for example, hygiene products, coal dewatering, farming (Zohuriaan-mehr and Kabiri, 2008), wastewater treatment, food additives, disposable diapers (Zohuriaan-mehr and Kabiri, 2008), pharmaceuticals and biomedical applications (Casquilho *et al.* 2013), (Wang *et al.* 2010), (J. Akhter, 2004), (Dafader, 2009). The hydrogel were

used as water adsorbents in agriculture field to increase soil absorption and water holding capacity (Zohuriaan-mehr and Kabiri, 2008) and these characteristic are very essential to experience the effect of dehydration and minimize the effect of drought stress in crops (J. Akhter, 2004). Utilization of hydrogels in cultivation has been identified in many studies. Further, by addition SAP in soil can enhance water storage feature of permeable soil to slow down the rates of eternal shrivelled under intense evaporation. Therefore, by increasing the uses of SAP in farming can reduce the need for dewatering systems of various types of plants due to capability of SAP to holding large quantities of water. In addition, the characteristic of SAP as controlled release system to assist the absorption of nutrients component, to sustain firmly and to slow down the nutrients form dissolving. Accordingly, the plant can gain all the nutrients and improved their development and germination rates (Zohuriaan-mehr and Kabiri, 2008). Besides, natural hydrogels were substitute to synthetic types because of some advantages which are large water absorption content, long lasting services life and numerous of raw chemical resources.

METHODOLOGY

Material

Kenaf fiber was obtained from Lembaga Kenaf and Tembakau Negara (LKTN), Indera Mahkota in Pahang, Malaysia. Acrylic Acid (AAc), Sodium Hydroxide (NaOH), N,N'-methylenebisacrylamide (NMBA) and Ammonium Persulfate (APS) were purchased from Sigma-Aldrich.

Production of Carbonaceous kenaf Fiber from HTC Process

Kenaf fiber was processed to a small length in ranging of 15cm to 20cm before grinding to fine pieces (550-600µm). This is to promote the effectiveness of mixing Kenaf fiber during conversion to hydrochar via HTC process. Hydrothermal technique was used in order to synthesize carbon particles. Hydrothermal process was operating in a pressure vessel for constant temperatures at 225 °C for 6hours. Distilled water was added during hydrothermal process to ensure the raw materials is submerged to allow subcritical water condition. The mixture was keep stirring with agitation speed of 50 rpm until the required time finished. The stirring process need to make sure the mixture is homogenously involved in the process. Subsequently, the products undergo filtration process after temperature of reactor dropped to room temperature. Product was dried in oven at 105°C for 24 hours before kept in airtight container for characterization purpose.

Synthesis of Superabsorbent Carbonaceous Kenaf fiber (SPC) by graft polymerization techniques

Superabsorbent porous carbonaceous particles were synthesized using graft polymerization technique. The 250ml of five-neck flask equipped with a magnetic stirrer, reflux condenser, nitrogen line and a thermometer. The flask was immersed in a water bath system and heated up to 70°C. Recent, prepared 12ml of Sodium Hydroxide (NaOH) and 8ml of Acrylic Acid (AAc) with 20ml of distilled water in different measuring cylinder respectively. Then, added the solution under continuous stirring. The calculated amount of carbonaceous fiber was added and at the same time nitrogen gas was supplied to the flask. After that, the amount of cross-linker NMBA was added to mixture and the mixture was stirred for 15 minutes. Subsequently, the gelatin was formed around 5 minutes reaction after APS initiator was added to the mixture. The gel was washed using distilled water and dried in oven for 24 hours at 105°C. Lastly, the dried gel was milled to particles size of 40-60 mesh and keep in the air tight container for testing purpose.

Characterization

The morphologies of SPC were synthesized by Scanning Electron Microscopy (SEM) and the present of functional groups of SPC were analysed by Fourier Transform Infrared Spectroscopy (FTIR).

Water Absorbency Measurement

Water absorbency of SPC was evaluated by using Tea-bag method. Deionize water were used as a medium to test water absorbency of SPC. 0.4g of SPC particles were weighing and immersed in deionize water at 30 minutes in the first period and followed the next 15 minutes until equilibrium reached. Afterward, the tea-bag was allowed to drain for a minutes to rinse off non-absorbed water. Water absorbency was calculated using equation (1):

$$Water\ Absorbency, Q\left(\frac{g(H_2O)}{g\ sample}\right) = \frac{m_2 - m_1}{m_1} \quad (1)$$

m_1 = initial weight of tea bag before immerse in the water,
m_2 = weight of tea bag after reach equilibrium,

RESULT AND DISCUSSION

Water Absorbency

The effect of percentage of carbon filler in water absorbency of SPC was listed in Table-1.

Table-1. The effect of percentage carbon filler in water bsorbency in SPC.

Code	Percentage of carbon filler (%)	Average Water Absorbency of SPC (g water/g sample)
MBA0.01 (Control Sample)	0	159.92
MBA0.01-C0.1	0.1	166.25
MBA0.01-C0.2	0.2	177.42
MBA0.01-C0.3	0.3	186.04
MBA0.01-C0.4	0.4	208.04
MBA0.01-C0.5	0.5	237.15

Table-1 showed that the water absorbency of SPC increased from 166.25 to 237.15 g water/g sample as the percentage of carbon filler increased from 0.1 to 0.5wt%. The higher of water absorbency is MBA0.01-C0.5 at 237.15 g water/g sample with 0.5wt% of carbon filler while the lowest water absorbency is MBA0.01 at 159.92 g water/g sample with 0.0wt% of carbon filler.

Figure-1 offers a clear view the trend of the graph between water absorbency of SPC against the percentage of carbon filler. As can see from the figure, the trend of the graph is proportionally increased between water absorbency of SPC with the percentage of carbon filler. At 0.5wt% carbon filler, the highest value of water absorbency of SPC was plotted. This is can be predicted that at this percentage of carbon filler is the best percentage to get the optimum value of SPC to absorb water. Other than that, the higher value of water absorbency found for MBA0.01-C0.5 than for control sample is explained by the much higher hydrophilicity of carbon component inside SPC which exhibit ionic groups to absorb water. Consequently, the water molecules form hydrogen bonds with the hydrophilic groups of the SPC leading to the steady shell of hydration around these hydrophilic groups resulting in the greater absorption of water. The result of water absorbency can be compared to hydrogel without carbon filler is much lesser than hydrogel with high percentage of carbon filler. At 0.1 and 0.2wt% of carbon filler does not give much effect on the water absorbency due to a small amount of carbon. Besides, the resultant copolymeric hydrogel was not cross-linked and after swelling it converted into a viscous liquid with water. In addition, as the time swelling is increasing over optimum level, porous network of SPC became fully saturated with no place of water molecules.

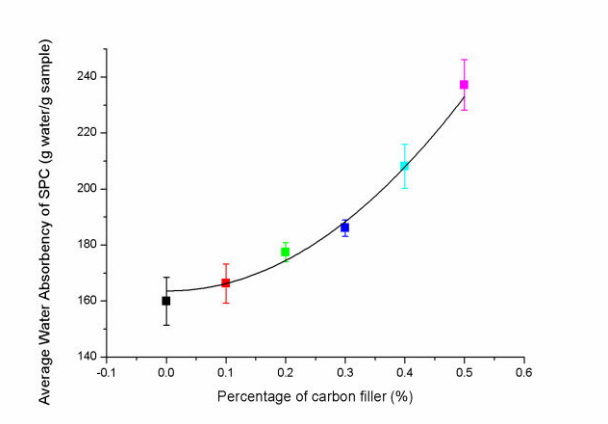

Figure-1. Average water absorbency of SPC against percentages of carbon filler.

Scanning Electron Microscopy (SEM)

Figure-2 shows the SEM images of the surfaces of the SPC samples. Obviously, Figure-2b and Figure-2c the surface morphology is smooth indicate that this structure is not suitable for the penetration of water into polymeric network. As can be seen form the Figure-2e and Figure-2f the surface of samples were multi layered and wrinkled. This surface morphology structurally increased the surface area of SPC. Thus, SPC were able to absorb and holding water rapidly when immersed in the solution. Furthermore, hydrogel that has multi layered surface is the regions of water permeation and interaction sites of external stimuli with hydrophilic groups of the graft copolymers.

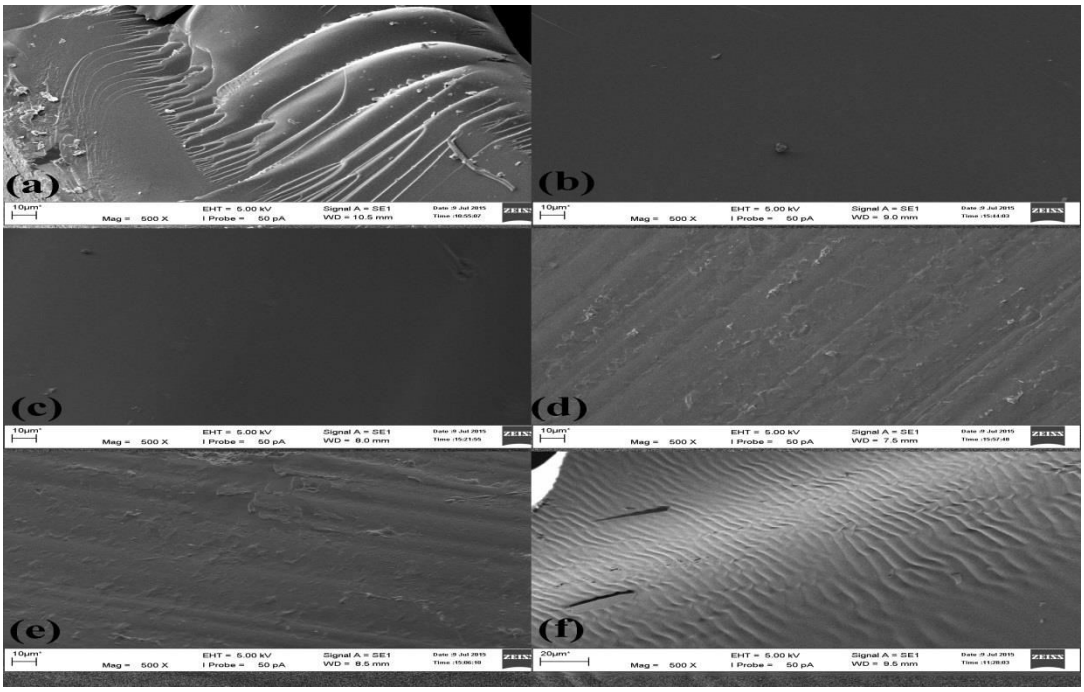

Figure-2. Scanning electron microscopy picture of SPC: (a) MBA0.01, (b) MBA0.01-C0.1, (c) MBA0.01-C0.2, (d) MBA0.01-C0.3, (e) MBA0.01-C0.4 and (f) MBA0.01-C0.5.

Fourier Transform Infrared Spectroscopy (FTIR)

Figure-3 shows the representative FTIR spectra of the SPC and control samples. The strong peaks appearing in the region of wavelength 3400-3100cm^{-1} are due to O-H stretching vibration. The characteristic bands of the cross-linked SPC were located at 1730-1700cm^{-1} assigned to the stretching vibrations of the C=O bond in carboxylic acids groups. Besides, the absorption peaks at 2950-2800cm^{-1} indicates the present of C-H stretching. The characteristic of amides groups which is N-H bend appear at 1640-1500cm^{-1}. Additionally, the absorptions band at 1320-1049cm^{-1} assigned to the stretching vibrations of the C-O bond. Moreover, at 770-710cm^{-1} represents the weak band of N-H from amide functional groups.

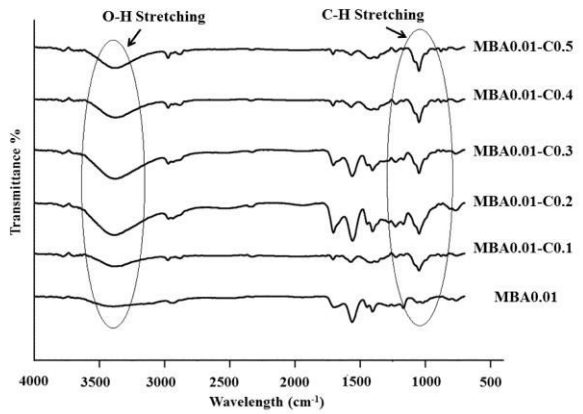

Figure-3. Fourier transform infrared spectroscopy (FTIR) characteristic of the SPC.

CONCLUSIONS

A high water absorbency superabsorbent carbonaceous fiber (SPC) based on Kenaf carbonaceous fiber was successfully prepared by using graft polymerization techniques. The highest water absorbency was recorded (219.65 g water/g sample) at MBA0.01-C0.5 with 0.5wt% carbon filler. The result confirmed that the carbonaceous fiber has cross-linked with the polymer chain as the increasing of carbon filler will give greater values of water absorbency. Besides, the FTIR spectra showed the formation of carbon component by exhibit all the characteristic bands in SPC. SEM testing also viewed the multi layered and wrinkled surface which contribute the higher absorption of water.

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