

Swelling Behaviors and Characterization of Oil Palm Empty Fruit Bunch-*Graft*-Poly (Acrylamide) Superabsorbent Polymer Composites

(Sifat Pembengkakan dan Pencirian Komposit Polimer Penyerap Lampau Serabut Tandan Kosong Buah Kelapa Sawit Cangkukan Poli (Akrilamida))

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ABSTRACT

The development on a class of technologically advanced materials like superabsorbent polymer composites (SAPC) involved multidisciplinary research started when its potential is recognized. Oil palm empty fruit bunch-graft-poly (acrylamide) (OPEFB-g-PAAm) SAPC was synthesized via simultaneous crosslinking and graft copolymerization of acrylamide (AAm) monomer onto OPEFB backbone with N,N'-methylenebisacrylamide (MBA) and ammonium persulphate (APS) acts as crosslinker and initiator, respectively, along with neutralization using solution polymerization method. Systematically, variables that affect the swelling behaviors of OPEFB-g-PAAm SAPC were optimized. The effects of initiator, crosslinker and filler concentration as well as solvent quantity and the degree of neutralization on water absorbency of OPEFB-g-PAAm SAPC were studied. Maximum absorbency of OPEFB-g-PAAm SAPC was achieved at 589.06 g/g when the amount of APS and MBA were 1.5 wt.% and 0.15 wt.%, respectively, and the OPEFB loading was at 10 wt.%. The optimum amount of solvent used was 15 mL and the degree of neutralization was 20%. The chemical structure of the OPEFB-g-PAAm SAPC was characterized by means of Fourier transform infrared (FTIR) spectroscopy. A mechanism pathway in synthesizing OPEFB-g-PAAm SAPC was suggested.

Keywords: Characterization; oil palm empty fruit bunch; poly (acrylamide); superabsorbent polymer composites; swelling behavior

ABSTRAK

Pembangunan bahan termaju seperti polimer komposit penyerap lampau (SAPC) telah berkembang pesat di dalam pelbagai aktiviti penyelidikan semenjak kelebihannya diketahui umum. Serabut tandan kosong buah kelapa sawit-cantum-poli (akrilamida) (OPEFB-g-PAAm) SAPC telah disintesis melalui proses pemaunsilangan dan pengkopolimeran cantum monomer akrilamida (AAm) ke atas tulang belakang OPEFB dengan menggunakan N,N'-metilenabisakrilamida (MBA) dan ammonium persulfat (APS) yang masing-masing berfungsi sebagai pemaunsilang dan pemula, bersama-sama peneutralan dengan menggunakan kaedah pempolimeran larutan. Pembolehubah seperti kuantiti pemaunsilang, pemula, pengisi, pelarut dan darjah peneutralan yang mempengaruhi sifat pembengkakan OPEFB-g-PAAm SAPC telah diperhatikan dan dioptimumkan secara sistematik. Penyerapan maksimum OPEFB-g-PAAm SAPC adalah 589.06 g/g apabila kuantiti APS, MBA dan OPEFB adalah masing-masing pada 1.5 wt.%, 0.15 wt.% dan 10 wt.%. Manakala, jumlah pelarut dan darjah peneutralan yang telah digunakan adalah 15 mL dan 20%. Struktur kimia OPEFB-g-PAAm SAPC telah dicirikan dengan menggunakan spektroskopi jelmaan Fourier infra-merah (FTIR) dan mekanisme dalam mensintesis OPEFB-g-PAAm SAPC telah dicadangkan.

Kata kunci: Serabut tandan kosong buah kelapa sawit; pencirian; poli (akrilamida); polimer komposit penyerap lampau; sifat pembengkakan

INTRODUCTION

Predominantly consist of loosely crosslinked polyelectrolyte, superabsorbent polymers (SAPs) are three-dimensional networks of flexible polymer chains that carry dissociated and ionic functional groups which characterized by hydrophilicity. These water insoluble materials possess the capability to absorb, swell and retain high capacity of fluids like water, brines and biological fluids, many times than their original weight by forming a gel. Among many others, AAm is the most frequently used nonionic monomer in preparing SAPs (Zhang et al. 2006). This is due to its

better salt resistance performance, high capability for water absorption and biocompatibility with physiologic body fluids (Marandi et al. 2008).

However, synthetic polymer based SAPs like AAm are poor in degradability especially for applications in agriculture and horticulture, though, they alone do have large fluid absorbing capacities (Xie & Wang 2008). Therefore, extensive attention has been directed towards SAPs being prepared through graft copolymerization of monomers onto the chain of such natural fibres to render the SAPs to be biodegradable, and hence producing

environmentally friendly SAPC, which may offer advantages for such applications.

The conventional method of burning OPEFB for disposal purpose often creates environmental problems in that it generates severe air pollution. Thus, economic utilization of OPEFB in turning its abundant supply from oil palm industry by-products into value-added products will be beneficial. According to Ibrahim et al. (2005), grafting of vinyl monomer such as AAm onto OPEFB backbone may be used to modify and improve various properties in the original vinyl polymer such as elasticity, absorbency, ion exchange capabilities, thermal resistance and hydrophilicity. Therefore, the objectives of this paper is to synthesis OPEFB-g-PAAm SAPC and to study the characteristic and swelling behavior of synthesized OPEFB-g-PAAm SAPC. The synthesized SAPC has benefited the system in enhancing the swelling ability while reducing the production cost and accelerate the generation of new materials for special applications.

MATERIALS AND METHODS

RAW MATERIALS

Chemicals such as AAm, MBA and APS purchased from Sigma-Aldrich were directly used as received. Meanwhile, OPEFB purchased from Sabutek Sdn. Bhd., Teluk Intan, Perak, was first ground to less than 100 μm sizes using a laboratory scale grinder machine before been washed twice with hot distilled water and then with acetone. The washed OPEFB fibre was then dried in an oven at 50°C for about 24 h to constant weight before been used.

OPEFB-GRAFT-PAAm SAPC SYNTHESIS PROCESS

A series of formulations with fixed amount of AAm and different amounts of OPEFB, crosslinker, initiator and distilled water as solvent with different degrees of neutralization were prepared by the following procedure. A synthesis apparatus with 500 mL five-neck round-bottom flask equipped with a stirrer, a condenser, a thermometer and a nitrogen line was set up in a water bath. Once the water bath temperature reaches 60°C, an amount of AAm monomer, MBA crosslinker, APS initiator and OPEFB were mixed together in a flask filled with distilled water and NaOH (2M) solution. The mixture solution was stirred vigorously and dissolved oxygen was flushed out from the system by purging nitrogen gas until the entire process was completed. The polymerization condition was set to be at 60°C for a period of 15 min. Once the polymerization process was completed, the product was filtered and washed with excess distilled water several times to remove any unreacted monomers and base. The product was then dried in an oven at 80°C until constant weight before milling. The resulting powder of OPEFB-g-PAAm SAPC was stored in a desiccator to avoid any moisture contact.

WATER ABSORBENCY MEASUREMENT

A series of tea bags containing an accurately weighed dry sample (0.1 ± 0.001 g) were immersed in 200 mL of distilled water at room temperature for a period of 24 hours. Swollen samples were then separated from unabsorbed water by filtering and hung up for 15 min until no liquid was dropped off from the sample. The water absorbency, Q of samples was calculated according to following equation:

$$Q = (m_2 - m_1) / m_1 \quad (1)$$

where m_1 and m_2 are the weights of the dry sample and the swollen sample, respectively. Q was calculated as grams of water per gram of dry hydrogel (g/g).

FOURIER TRANSFORM INFRARED (FTIR) SPECTROSCOPY

The IR spectra of the OPEFB, PAAm SAPs and OPEFB-g-PAAm SAPC samples were recorded on Fourier Transform Infrared Spectrometer using KBr disk pellets technique. The spectra were recorded in the range of 4000 to 370 cm^{-1} .

RESULTS AND DISCUSSION

WATER ABSORBENCY CAPACITY:

Effect of Crosslinker The amount of MBA was varied from 0.10 wt.% to 0.30 wt.%. The influence of crosslinker loading on water absorbency of SAPC systems is shown in Figure 1. From Figure 1, it is obvious that crosslinker loading at 0.15 wt.% resulted in the maximum water absorbency of 589.06 g/g for the synthesized SAPC. When the crosslinker amount was over 0.15 wt.%, the water absorbency was sharply decreased. Noticeably, a higher concentration of crosslinker will developed a larger number of growing polymer chains by the generation of more crosslink points that caused the formation of an additional network (Wu et al. 2003). Thereby, water absorbency decreased with the increase in crosslinker concentration due to the available free volume within the SAPC system which gets diminished and less water molecules can enters the SAPC network structure (Wu et al. 2003). Similar clarification has also been supported by other researchers (Li et al. 2005; Li et al. 2007).

In contrast when the concentration of the crosslinker is lower than 0.15 wt.%, the water absorption capacity of the SAPC was low too; as the low crosslinking SAPC is unable to maintain the absorbed water and may be dissolved easily when it was immersed in water. The results may be due to the fact that the cross-linkage network of the SAPC cannot be formed efficiently because of few crosslink points (Li et al. 2005; Wu et al. 2003; Li et al. 2007). Under these experimental conditions, the concentration of the crosslinker should be higher than 0.10 wt.%, because lower than that, such samples was semisoluble and almost represent as sol-gel state in water, where water cannot be

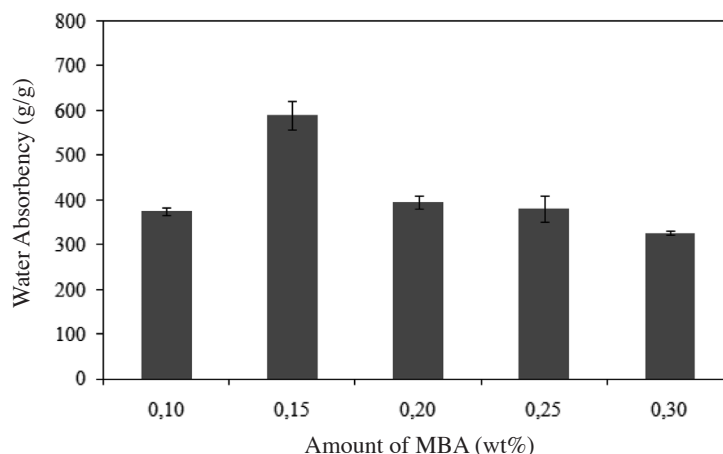


FIGURE 1. Effect of crosslinking on water absorbency

ted in the network, and the water absorbency can hardly be measured.

Effect of Initiator The effect of the amount of APS on water absorption capacity of the prepared SAPC was studied from 1.0 wt% to 3.0 wt% loading, and the results can be seen in Figure 2. It can be seen that with the increase in the content of initiator, the water absorbency of the OPEFB-g-PAAm SAPC also increased, and reached a maximum of 589.06 g/g at an APS content of 1.5 wt%. However, further increase in APS resulted in a decline of water absorbency of the SAPC produced.

From Figure 2, the increase in the amount of initiator from 1.0 wt% to 1.5 wt% results in an increase in water absorbency, likely, because more graft polymerization occurred and more stable network structures were formed in the synthesized SAPC. As interpreted by Li et al. (2005) and Li et al. (2008), at low content, the initiator were mostly utilized in producing a large number of free-radical sites on the OPEFB backbone at which the AAm monomers could be grafted. Therefore, the grafting yield increases the grafted points and, in turn, the absorbency of the graft

polymer increased with the increase in initiator content (Li et al. 2005; Li et al. 2008). Besides, theoretically, when the concentration of the initiator is below 1.5 wt%, the graft polymerization reaction is in the slower rate, where it results in less polymer network. Thus, the water absorbency obtained is lower than 1.5 wt% (Wu et al. 2003).

On the other hand, once the initiator concentrations increase from 1.5 wt% to 3.0 wt%, the polymerization reaction rates was faster, the mean kinetic chain length was decreased and the smaller polymer network space due to the generation of more radical which results in the termination of growing chains, which lead to the decrease of water absorbency of the synthesized SAPC (Wu et al. 2003; Singha et al. 2008; Yu et al. 2009). According to Ibrahim et al. (2005), initiator in the presence of heat decomposes into SO_4^- radical which is involved in the generation of OPEFB fibre radical. Increasing the amount of initiator increased the free radical which enhances the possibility of initiating reactive site on the OPEFB fibre where PAAm can be grafted (Ibrahim et al. 2005). Above a critical content of 1.5 wt%, the excess initiator was utilized in the homopolymerization of AAm monomers

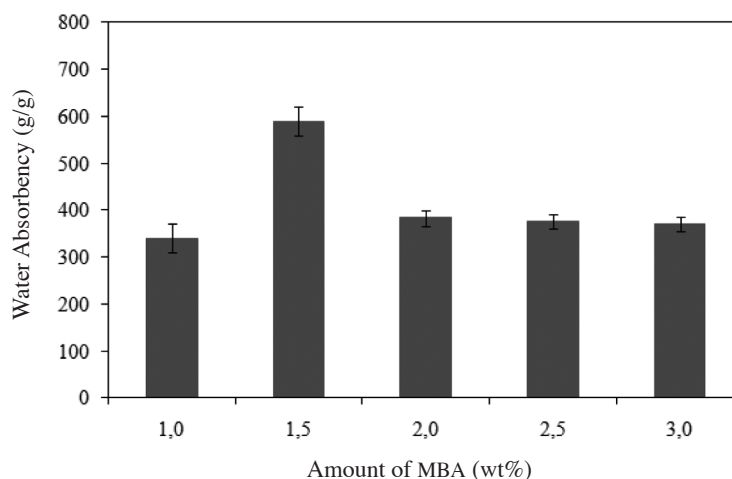


FIGURE 2. Effect of initiator on water absorbency

and the termination of OPEFB fibre radicals become more significant.

Effect of Solvent The effect on the volume of water used as solvent in synthesizing the SAPC was studied by varying the volume from 5 mL to 25 mL. As shown in Figure 3, the maximum water absorbency of OPEFB-g-PAAm SAPC of 589.06 g/g, was achieved when the volume of solvent in the reaction system was around 15 mL. Basically, the volume of solvent affects the reactants concentration which directly affected the water absorption capacity of the polymer (Yu et al. 2009). At low water volume, i.e. below 15 mL, the solvent was insufficient to completely dissolve the required amount of AAm and OPEFB. Therefore, the concentrations of the reactants were very high which actually has increased the rate of polymerization and crosslinking reaction, and resulted mean kinetic chain length became shorter and polymer network space became smaller. Consequently, the water absorbency of the SAPC obtained at low solvent volume was decreased (Yu et al. 2009).

However, when the volume of water in the reaction system was increased, the concentrations of the crosslinking

agent, the initiator, and the monomer were all decreased. As a result, the rates of polymerization and crosslinking reaction were slowed down, and hence, less polymer network. Inevitably, the water absorption capacity of the SAPC was decreased too (Yu et al. 2009). In addition, when the amount of the solvent increases, the percentage of grafting was also decreased due to the free movement of the monomer molecules in the relative large volume of reaction mixture, hence, the interaction between the monomer was reduced (Ibrahim et al. 2005).

Effect of Degree of Neutralization The effect of degree of neutralization on water absorbency of the synthesized SAPC in distilled water is shown in Figure 4. As shown in Figure 4, the water absorbency increased with the increase of degree of neutralization from 10% to 20% and decreased with further increase up to 40%.

Once the AAm monomer was neutralized with NaOH, the amide groups on the side chains of grafted PAAm SAPC has turned into carboxylate group, which possess higher hydrophilicity than the amide group (Gao et al. 2008; Li et al. 2005; Zhang et al. 2006). The negatively charged

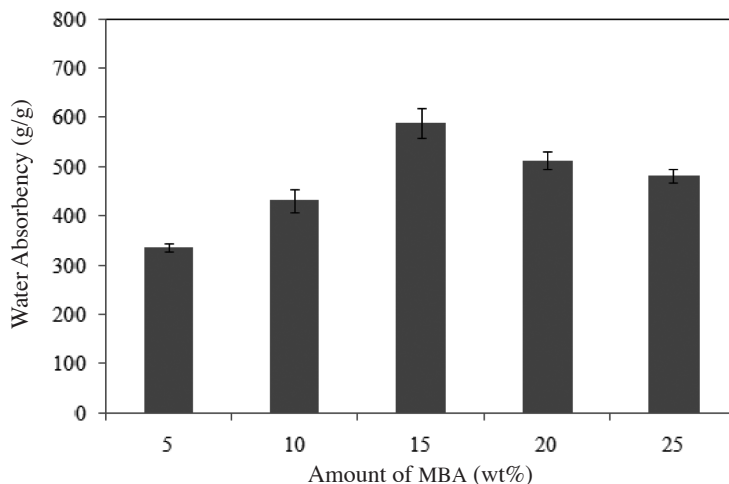


FIGURE 3. Effect of solvent on water absorbency

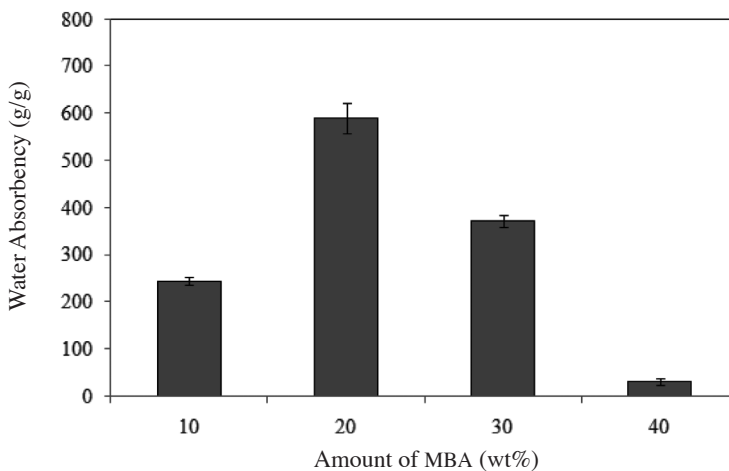


FIGURE 4. Effect of degree of neutralization on water absorbency

carboxyl groups attached to the polymer chains set up an electrostatic repulsion, which tended to expand the network of the swollen SAPC. In a certain range of molar ratio, the electrostatic repulsion, ionic hydrophilic property and osmotic pressure difference increased with the increases of degree of neutralization, resulting in the increase of water absorbency (Li et al. 2005).

Further increase in the degree of neutralization results in the generation of more sodium ions in the polymeric network, which reduces the electrostatic repulsion and increases the chain stiffness by screening the negative charges of the carboxyl groups, thus resulting in a decrease of water absorbency. The chains could expand to such an extent that the distance between neighboring charges became too high for optimum cooperation effects between the charges (Li et al. 2005).

Effect of Filler Figure 5 shows the influence of OPEFB content on the water absorbency for the synthesized SAPC. It can be seen that the water absorbency of SAPC incorporated with 10 wt% OPEFB, absorbed almost the same amount of water with PAAm SAPs. OPEFB work as another crosslinking point besides as biodegradable material that exists in the synthesized SAPC system. At 5 wt% of OPEFB, the amount of OPEFB does not provide enough crosslinking point within the SAPC polymeric network space; thus, the water absorption capacity was lowered. However, as the loading increases near 10 wt%, the ability of water absorbency was enhanced, due to the OH molecules on the OPEFB backbone could react with AAm monomer, which benefit the system by forming a network structure. When the amount of OPEFB is suitable for the system; i.e. 10 wt% OPEFB, the crosslink density and the network space of the SAPC were almost similar to that pristine ones resulting in almost the same capacity in water absorbency.

Further increase in OPEFB amount from 10 wt% to 15 wt% remarkably decreased the elasticity of SAPC, and hence reduced the ability in water absorbency. The

decreasing tendency of water absorbency with increasing OPEFB content may be attributed to the fact that additional OPEFB fibre in the SAPC system results in the generation of more crosslink points in the polymeric network. OPEFB in the network structure has a lot of hydroxyl groups to form superfluous network point, which increases the network density of the composite where it leads to a more difficult permeation of water into the SAPC system.

SPECTRAL CHARACTERIZATION AND PROPOSED MECHANISM

FTIR spectra of OPEFB and OPEFB-*g*-PAAm SAPC are shown in Figure 6. Both spectra show a characteristic broad absorption band of the hydroxyl group around 4000-3200 cm^{-1} . This could be attributed to O-H stretching vibrations of cellulose, absorbed water, hemicellulose and lignin constituent of OPEFB (Ibrahim et al. 2003a). The presence of one additional peak around 3609.92 cm^{-1} in the OPEFB-*g*-PAAm SAPC spectrum indicates the existence of an amide groups from AAm structure after the grafting process.

The C=C and C=O stretching of carbonyl groups which exist in the aromatic rings in hemicellulose and lignin in OPEFB, and C=O asymmetric stretching of carboxylate anions that presence in amide functional groups in the SAPC network seems to be appeared at the same broad absorption band of around 1700-1600 cm^{-1} (Ibrahim et al. 2003a; Ibrahim et al. 2003b; Ibrahim et al. 2005). These trends of absorption band were reconfirmed by the shape of the signal around 4000-3400 cm^{-1} which was related to the O-H stretching of the carbonyl groups and the symmetric stretching mode of carboxylate anions, respectively.

According to Ibrahim et al. (2003a), the aliphatic and aromatic groups in the plane deformation vibration of methyl, methylene and methoxy groups in OPEFB can be seen near 1412-1110 cm^{-1} . The synthesized OPEFB-*g*-PAAm SAPC comprises OPEFB backbone grafted with PAAm that carry both amide and carboxylate as functional groups,

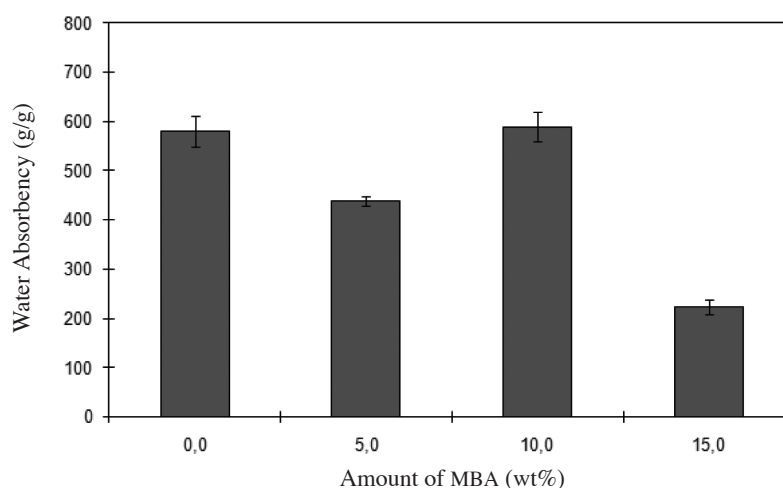


FIGURE 5. Effect of filler on water absorbency

and was shown in the peak around 1052-1032 cm^{-1} which is due to the C-O-C bonding between OPEFB and the side chains. Quantitatively, the grafting in these regions could be proved from the observation that the absorbency peak was reduced. Another evidence of grafting could be seen from the peaks that appeared after 1000 cm^{-1} which were due to the stretching of the $\text{CH}_2\text{-CH}_2$ groups (Ibrahim et al. 2003b). Since the OPEFB-g-PAAm SAPC spectrum shows

the same absorption band that presence both in OPEFB and PAAm SAPs, the spectrum strongly provides evidence that grafting process between PAAm and OPEFB in OPEFB-g-PAAm SAPC has successfully taken place.

The proposed mechanism for crosslinking graft polymerization of AAm onto OPEFB backbones in the presence of APS and MBA is shown in Figure 7. In the first step, the thermally dissociating initiator, i.e. APS,

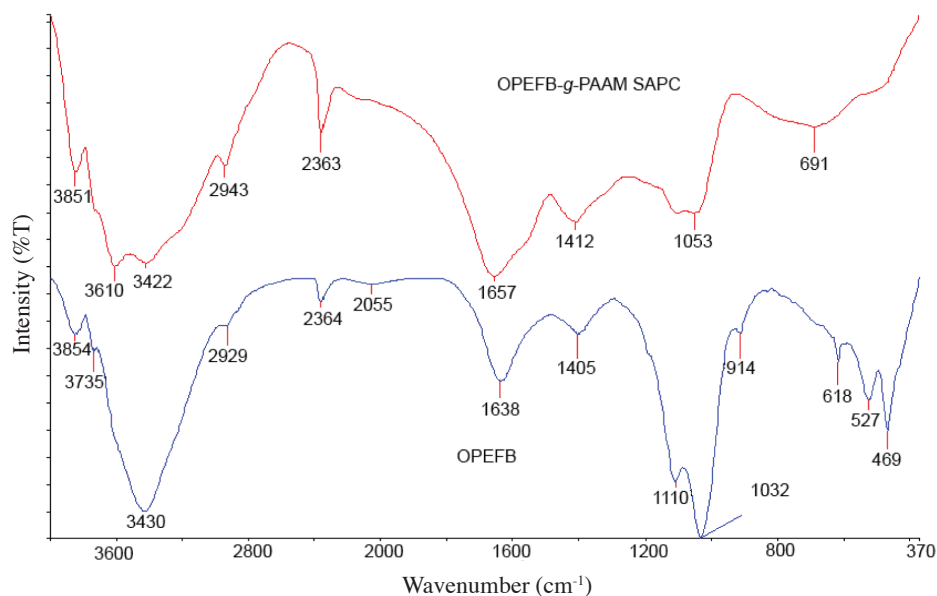


FIGURE 6. FTIR Spectra of the OPEFB and OPEFB-g-PAAm SAPC

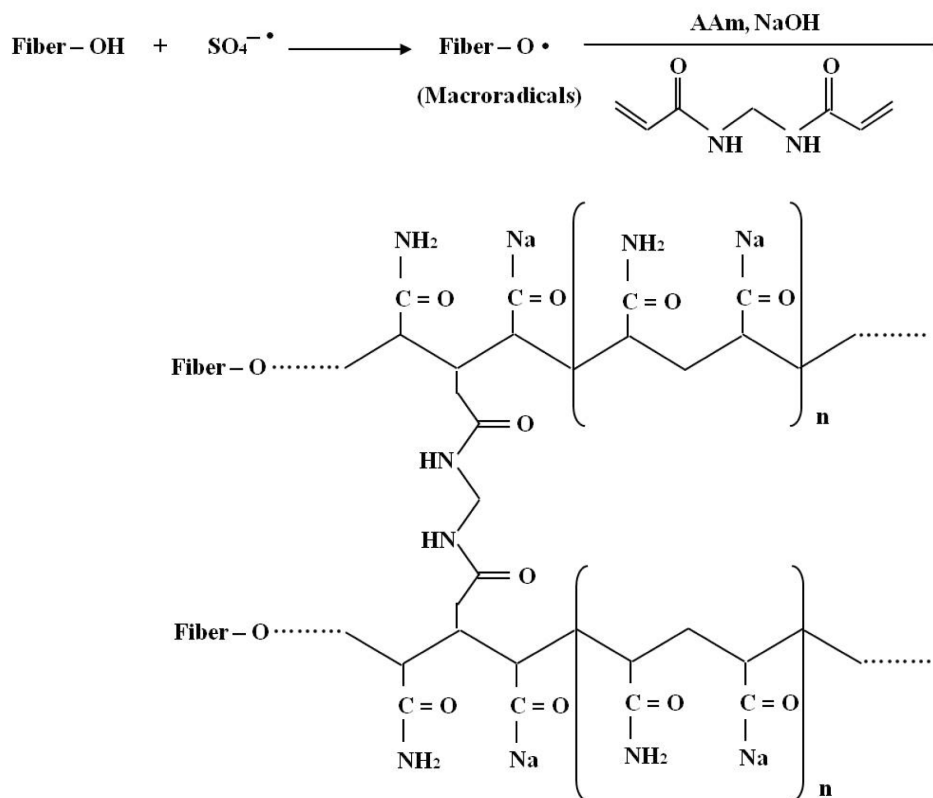


FIGURE 7. Proposed Mechanism Pathway for Synthesis of OPEFB-g-PAAm SAPC

was decomposed under heating (60°C) to generate sulfate radicals, which are well known as chain carriers. According to Singha et al. (2008), polymeric materials containing cellulose, -OH and C-H sites are the active centers for grafting of polymeric chains onto the natural fibres backbone. Thus, the radical abstracts hydrogen from one of the existing hydroxyl groups in the OPEFB backbone to form the corresponding macro-initiator, implying to the formation of alkoxy (C-O-C) radicals on the substrate.

These macro-radicals initiate a radical polymerization of AAm grafting onto the OPEFB backbone, which later the active centers of the cellulose backbone are radically liberating the graft polymerization. PAAm was believed to be grafted on the OPEFB surfaces. On the other hand, the hydrolyzed amide groups in PAAm which were converted into carboxylate groups during neutralization are carrying negative charges. These negatively charged groups are susceptible to the crosslinker; i.e. MBA. Thus, crosslinking occurs, and finally a three-dimensional network of SAPC was obtained, which may possess characteristics for both OPEFB and PAAm.

CONCLUSION

The effects of initiator, crosslinker and filler concentration as well as solvent quantity and the degree of neutralization on water absorbency of OPEFB-g-PAAm SAPC were studied. Maximum absorbency of OPEFB-g-PAAm SAPC was achieved at 589.06 g/g when the amount of APS and MBA were 1.5 wt% and 0.15 wt%, respectively, and the OPEFB loading was at 10 wt%. The optimum amount of solvent used was 15 mL and the degree of neutralization was 20%. The chemical structure of the OPEFB-g-PAAm SAPC was characterized by means of FTIR spectroscopy and a proposed mechanism pathway in synthesizing OPEFB-g-PAAm SAPC was also suggested. Therefore, the synthesis of OPEFB-g-PAAm SAPC has benefit the system in enhancing the swelling ability while reducing the production cost and accelerates the generation of new materials for special applications.

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