

## Characterization and Absorbing Properties of Oil Palm Empty Fruit Bunch Filled Poly (Acrylic Acid-co-Acrylamide) Superabsorbent Polymer Composites

(Pencirian dan Sifat-sifat Penyerapan Komposit Polimer Penyerap Lampau Tandan Kosong Kelapa Sawit Cangkukan Poli(Akrilik Asid-ko-Akrilamida))

NOR ERMA SHUHADAH ABDUL RAZAK, SHAHRIR HASHIM\* & ABDUL RAZAK RAHMAT

### ABSTRACT

*Oil palm empty fruit bunch graft poly (acrylic acid-co-acrylamide) superabsorbent composite (OPEFB-g-(PAA-co-PAM) SAPC) was synthesized by graft copolymerization of the acrylic acid (AA) and acrylamide (AM) comonomer onto OPEFB fibre using ammonium persulfate (APS) and N,N-methylene bisacrylamide (MBA) as an initiator and crosslinker, respectively. The absorbency in various chloride salt solutions indicated that the absorbency decreased with increasing ionic strength of the salt solutions. Moreover, the absorbency under load (AUL) of SAPC was investigated at various applied loading and results show that, AUL decreased with increasing applied loading. Infrared Spectroscopy (IR) and Thermogravimetric Analysis (TGA) were carried out to confirm the chemical structure and thermal properties of the synthesized superabsorbent, respectively.*

*Keywords: Absorbency under load; Graft copolymerization; OPEFB; superabsorbent composites; swelling behaviour*

### ABSTRAK

*Komposit polimer penyerap lampau (SAPC) tandan kosong kelapa sawit cangkukan poli(akrilik asid-ko-akrilamida) (OPEFB-g-(PAA-co-PAM) SAPC) disintesis melalui pengkopolimeran cangkuk oleh asid akrilik(AA) dan akrilamida (AM) komonomer kepada gentian OPEFB menggunakan ammonium persulfat (APS) dan N,N-methylen bisacrylamide (MBA) dengan masing-masing sebagai pemula dan pemaat silang. Kebolehserapan SAPC di dalam pelbagai jenis larutan garam dikaji dan keputusan menunjukkan bahawa kebolehserapan berkurang dengan pertambahan kepekatan ion. Disamping itu, kebolehserapan di bawah bebanan (AUL) dikaji pada pelbagai bebanan dan keputusan menunjukkan bahawa, AUL berkurang dengan pertambahan bebanan. Spektroskopi inframerah (IR) dan analisis termogravimetri (TGA) masing-masing digunakan untuk mengesahkan struktur kimia dan sifat terma SAPC.*

*Kata kunci: Kebolehserapan di bawah bebanan; komposit penyerap lampau; OPEFB; pengkopolimeran cangkuk; sifat pembengkakan*

### INTRODUCTION

Superabsorbent polymers (SAPs) are hydrophilic and three dimensional networks that exhibit the ability to highly swell in water, saline or biological fluids and retain significant fraction of the fluids within their structure but they do not dissolve in water (Buchholz & Graham 1998). SAPs have great advantages over traditional water absorbing materials such as cotton, pulp and sponge. They are widely used in sanitary goods such as disposable diapers and hygiene napkins. Besides, these materials can help conserve water in a variety of agricultural and horticultural applications by improving the water holding capacity of sandy soil.

Although superabsorbents made from synthetic polymers possess excellent characteristics, the limitations of these materials in comparison to natural based ones seem to be worth noting. In fact, their toxicity and non-biodegradability might pose long term environmental

problems and limit their uses. Therefore, modifications of natural materials such as starch (Fanta et al. 1979; Ibrahim et al. 2007; Weaver et al. 1977), cellulose (Abd El-Mohdy & Abd El-Rehim 2008; Demetri et al. 2008) and carrageenan (Ramazani-Harandi et al. 2006) have been utilized to prepare superabsorbent composites.

The desired features of SAPs are high swelling capacity, high swelling rate and high absorbency under load (AUL). The majority of reported SAPs possess only the first and second feature despite many efforts to synthesize SAPs in recent years which focused on improving other parameters. In this study, the filler used is derived from an oil palm tree component, namely empty fruit bunch (OPEFB). This material is a by-product of the palm oil industry. At the moment, no study has been done on OPEFB filled superabsorbent polymers. The superabsorbent composites based on AA and AM monomer was synthesized by graft copolymerization method.

## EXPERIMENTAL DETAILS

## MATERIALS

The OPEFB fibre used throughout this study was purchased from Sabutek (M) Sdn Bhd., Teluk Intan, Perak, Malaysia. The fibre was first ground to less than 75  $\mu\text{m}$ . After that, the fibre was washed twice with hot distilled water and then with acetone before drying in the oven for at 50°C before used. AA, chemically pure, (Merck) was distilled under reduced pressure prior to use to remove inhibitor. AM, chemically pure, (Merck) was used as purchased. APS as an initiator was supplied by Aldrich and MBA as a crosslinker was obtained from Aldrich. Sodium hydroxide (NaOH) as neutralization agent and saline solution sodium chloride (NaCl), calcium chloride ( $\text{CaCl}_2$ ) and aluminium chloride ( $\text{AlCl}_3$ ) were prepared with distilled water.

## PREPARATION OF SUPERABSORBENT BY GRAFT COPOLYMERIZATION

Superabsorbent composites were prepared through the graft copolymerization of OPEFB onto PAA-co-PAM in the presence of MBA and APS: Typically, 10 wt% of OPEFB was added to 20 mL degassed distilled water in a three-neck flask equipped with a stirrer, condenser, thermometer and nitrogen line. The flask was placed in a thermostated water bath to control the reaction temperature at 60°C. The oxygen in the slurry was then removed by passing nitrogen for 20 min. Then AA (50 wt%) was dissolved in 15 mL distilled water and neutralized to 60 wt% by addition of NaOH solution (2M). Afterwards, AM (50 wt%) was added to the above partial neutralized monomer solution. Under a nitrogen atmosphere, MBA (0.05 wt%) was added to the mixture. After stirring for 30 min, the mixed solution was heated to 60°C gradually, and then the initiator APS (0.60 wt%) was added into the flask. The polymerization reaction was allowed to proceed for 2 h with constant stirring speed under nitrogen atmosphere. After 2 h, the resulting product was washed several times with distilled water, dried at 60°C to a constant weight and then milled. The resulting superabsorbent composite powder was kept free from moisture, heat and light.

## CHARACTERIZATION

IR spectra of OPEFB and OPEFB-g-PAA-co-PAM SAPC was recorded using KBr pellets using a (Perkin Elmer Spectrum One, Nicolet 5700) spectrophotometer. Thermal stability of samples was studied on Perkin Elmer-TGA Thermal Analyzer with a temperature range of 35°C to 750°C at heating rate 10°C with nitrogen flow rate of 50 mL  $\text{min}^{-1}$ .

## ABSORBENCY IN VARIOUS SALINE SOLUTIONS (Q)

The dried samples of OPEFB-g-PAA-co-PAM SAPC (0.10 g) were placed in tea bags and immersed in 100 mL of NaCl,  $\text{CaCl}_2$  and  $\text{AlCl}_3$  with different concentration (0.009 w/w%, 0.09 w/w% and 0.9 w/w%) for 24h. The tea bags were hung up for 15 min to remove the excess solution and wiped

before measured. The weight of the tea bag and swollen samples ( $W_s$ ) was then measured, and the absorbency was calculated as follows:

$$\text{Absorbency } (Q, \text{ g/g}) = (W_s - W_d) / W_d \quad (1)$$

where  $W_s$  and  $W_d$  are the weight of the swollen gel and the dry sample, respectively. Absorbency is calculated as gram of water per gram of SAPC (g/g).

## ABSORBENCY UNDER LOAD (AUL)

A macroporous sintered glass filter plate was placed in a petri dish and a weighted dried sample was placed uniformly on the surface of polyester gauze located on the sintered glass. A cylindrical solid load was put on the dry sample while it can be freely slipped in a glass cylinder. The desired load (applied load 5, 10 and 15 N) was placed on the dry sample (Figure 1). Then, 0.9 wt.% saline solution was added so that the liquid level was equal to the height of the sintered glass filter.

The set was covered to prevent surface evaporation and probable change in the saline concentration. After 60 min, the swollen sample was weighted again, and AUL was calculated according to (1).

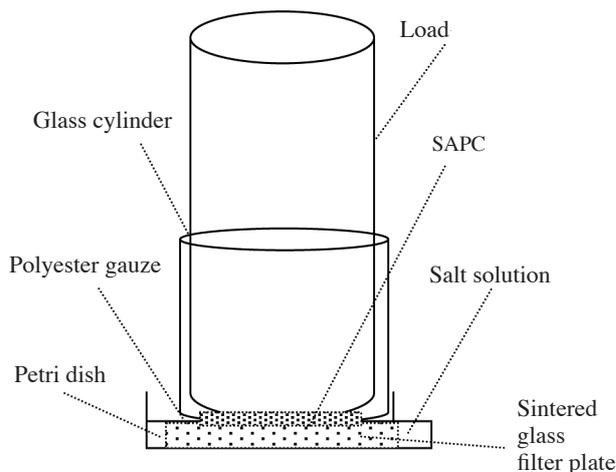


FIGURE 1. Scheme of the absorbency under load (AUL) tester

## RESULTS AND DISCUSSION

## FTIR ANALYSIS

The FTIR analysis was carried out to confirm the chemical structure of the prepared graft copolymer. Infrared spectra of (a) OPEFB and (b) PAA-co-PAM grafted OPEFB are shown in Figures 2(a) and (b), respectively. The band observed at 897  $\text{cm}^{-1}$ , 1053  $\text{cm}^{-1}$ , 1241  $\text{cm}^{-1}$  and 3100-3600  $\text{cm}^{-1}$  was attributed to D-galactose, anhydro-D-glucose, glycosidic linkage and stretching of O-H groups of non-modified OPEFB respectively. New peaks at 1713  $\text{cm}^{-1}$ , 1675  $\text{cm}^{-1}$  and 1447  $\text{cm}^{-1}$  corresponded to carboxylate and carboxamide

functional groups are evidence that AA and AM were grafted to the OPEFB. These peaks were attributed to  $\text{-C=O}$  stretching of carbonyl groups of acid moiety of AA unit,  $\text{COO}^-$  stretching of symmetrical and asymmetrical stretching mode of carboxylate groups and stretching of amide moiety of AM group. The stretching band of N-H overlapped with O-H stretching band of the cellulose portion of the copolymer. It can be summarized that the graft reaction has taken place among AA, AM and OPEFB. This confirms that both acrylate and acrylamide have been grafted onto the OPEFB.

#### ABSORBENCY IN VARIOUS SALT SOLUTIONS

The effect of ion type and concentration on absorbency capacity is shown in Figures 3 and 4, respectively. Figure 3 shows that for a given concentration of salt solutions, the water absorbency in NaCl solution was far higher than that of in  $\text{CaCl}_2$  and  $\text{AlCl}_3$  solution. This drastic decrease of water absorbency in multivalent cationic solution could be due to the complexing ability of the carboxylate or carboxamide groups inducing the formation of intramolecular and intermolecular complexes which resulted in an increase in the crosslinking density of

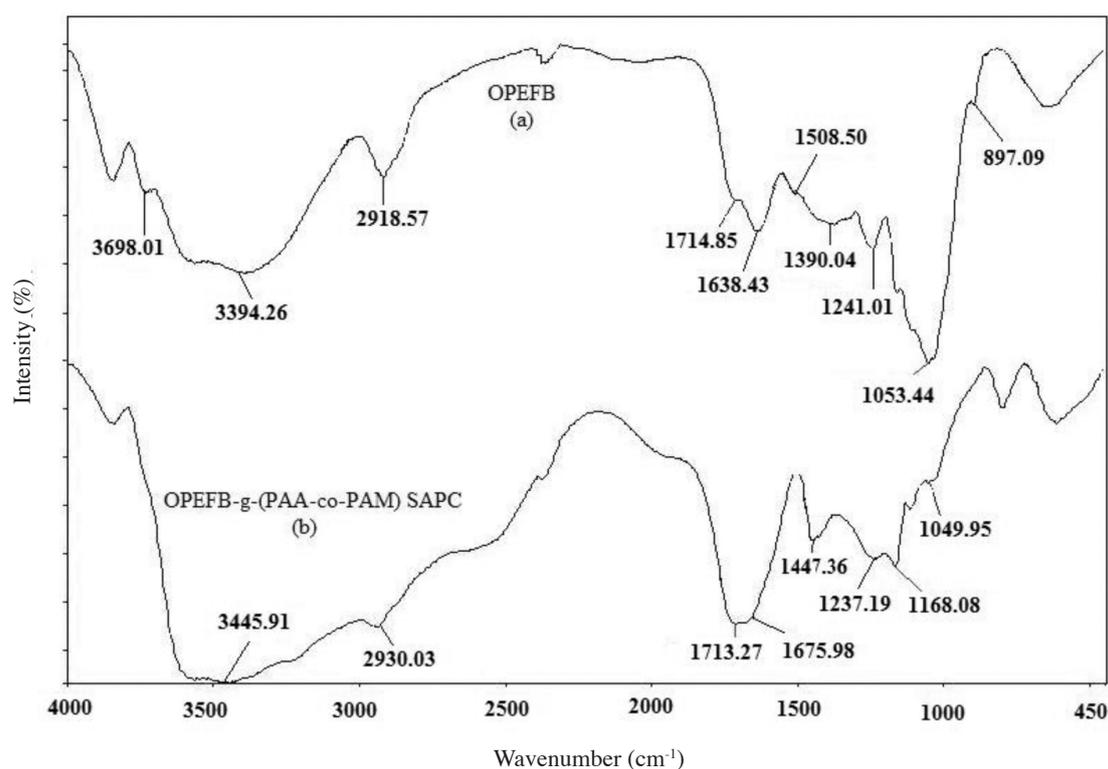


FIGURE 2. Infrared spectra of (a) OPEFB and (b) OPEFB-g-(PAA-co-PAM) SAPC wavenumber ( $\text{cm}^{-1}$ )

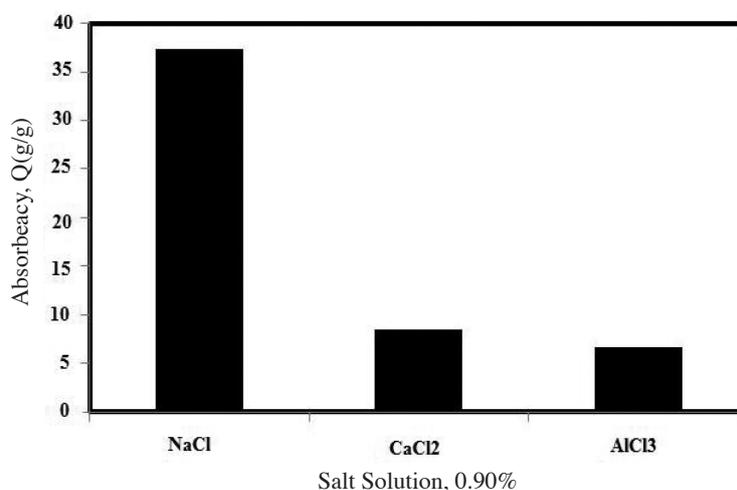


FIGURE 3. Absorbency of the OPEFB-g-(PAA-co-PAM) SAPC in various salt solutions

network (Castel et al. 1990). Therefore the absorbency for the SAPC in the salt solutions was in the order of  $\text{NaCl} > \text{CaCl}_2 > \text{AlCl}_3$ .

As shown in Figure 4, absorbing capacity not only depend on the type of salt solution but also on the concentration of the salt which is added to the swelling medium. These results reveal that the absorbency decreased with increasing ionic strength of the salt solution (Pourjavadi et al. 2006). For instance, absorbing ability of anionic hydrogels in various salt solutions is significantly decreased comparing to the absorbing values in distilled water. This sensitivity of salt has been attributed to the reduction of osmotic pressure difference between the gel network and the external solution. In additional, in the presence of cations, they shield the anion and prevent efficient electrostatic anion-anion repulsion. This well known undesired absorbing loss is often referred to as

charge screening effect. In the case of salt solutions with multivalent cations, ionic crosslinking at the surface of particle cause an appreciable decrease in absorbing capacity (Pourjavadi & Ghasemzadeh 2007).

#### ABSORBENCY UNDER LOAD (AUL)

When superabsorbents are under a load, the absorbing capacity is considerably reduced. Therefore, AUL is often defined and reported especially in technical data (Pourjavadi et al. 2007). Because AUL values logically change with the mechanical strength of the swollen gel proportionally, AUL can be considered a measure of the gel strength of the SAPC. As shown in Figure 5, the minimum time needed for the highest AUL in the case of each load was determined to be  $\sim 150$  min. After this time, the AUL values remained unchanged. In addition, AUL decreases

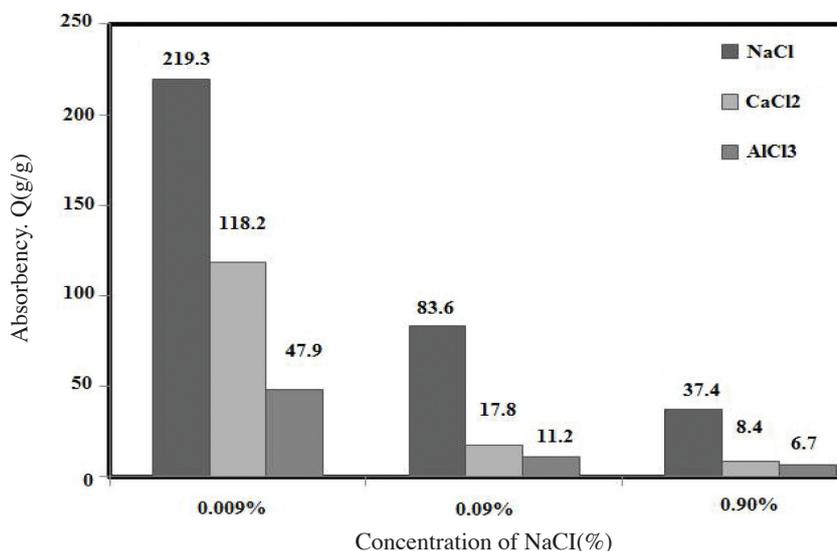


FIGURE 4. Absorbency of OPEFB-g-(PAA-co-PAM) SAPC in saline solution with various concentrations

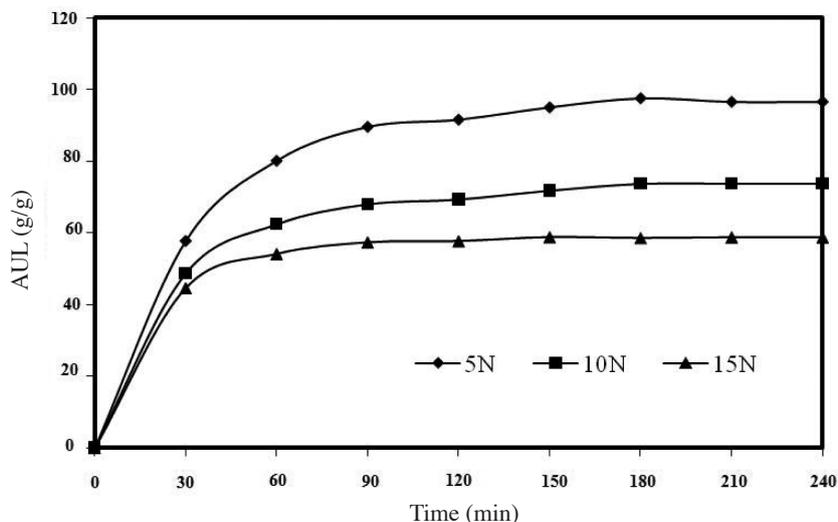


FIGURE 5. Time dependence of the AUL values for optimized OPEFB-g-PAA-co-PAM SAPC sample; MBA - 0.05 wt%, APS - 0.60 wt%, molar ratio of AM/AA - 50/50, neutralization percentage - 60 wt%

with the increase in loading as expected (Marandi et al. 2008 and Pourjavadi et al. 2006).

#### THERMOGRAVIMETRIC ANALYSIS (TGA)

Thermogravimetric analysis considered the most practical widely used method to illustrate the thermal stability of polymers over a wide range of temperature. Figure 6 and 7 show the thermogravimetric curves and the prepared derivatives respectively for (a) OPEFB, (b) PAA-co-PAM SAP and (c) PAA-co-PAM SAPC. It is observed that the grafted OPEFB show an enhanced thermal stability. Below 100°C, about 5% weight loss was observed in the ungrafted OPEFB. This may due to the dehydration of fibres. PAA-co-PAM SAP and PAA-co-PAM SAPC were thermally stable up to 200°C and slowly begin to decrease after that. The initial decomposition temperature increased from 271.43°C for OPEFB to 351.43°C for PAA-co-PAM SAP and 422.86°C for PAA-co-PAM SAPC.

In comparison to the maximum decomposition temperature of 363°C for OPEFB, the maximum decomposition temperature was shifted to 424°C for PAA-co-PAM SAP and 460°C for PAA-co-PAM SAPC. These observations clearly indicate that grafting improved the thermal stability of composite. In addition, PAA-co-PAM SAPC does not only show a higher thermal decomposition temperature but also give a lower weight loss rate in temperature range of 60 – 500°C. The results indicate that the introduction of OPEFB into PAA-co-PAM polymeric network enhances thermal stability of the superabsorbent composite. This may be attributed to the fact that the incorporation of OPEFB into PAA-co-PAM system improves the whole polymeric network owing to the generation of chemical bonds between OPEFB and the PAA-co-PAM polymeric network. Moreover, the grafted polymers entangle and form a crosslinked type of network, which when heated forms an insulative carbonaceous char barrier on the surface thus inhibiting degradation (Das et al. 1999).

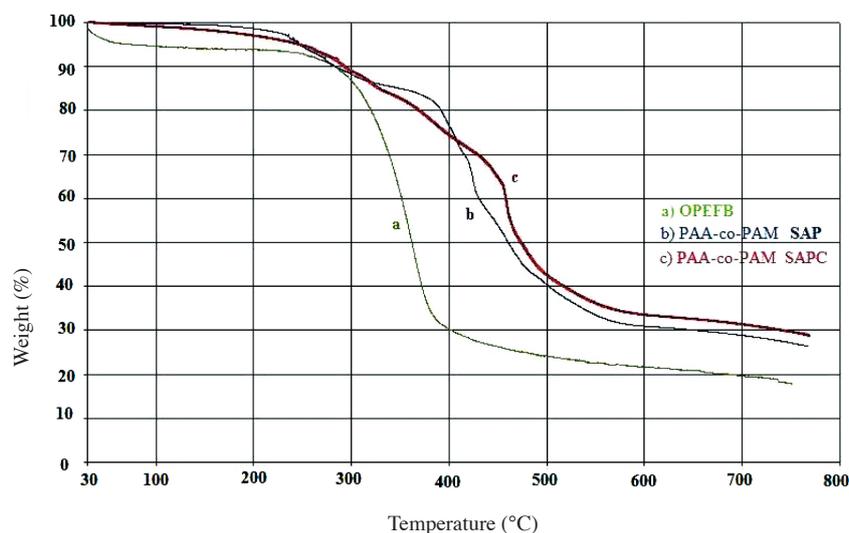


FIGURE 6. TGA thermogram of (a) OPEFB, (b) PAA-co-PAM SAP and (c) PAA-co PAM SAPC

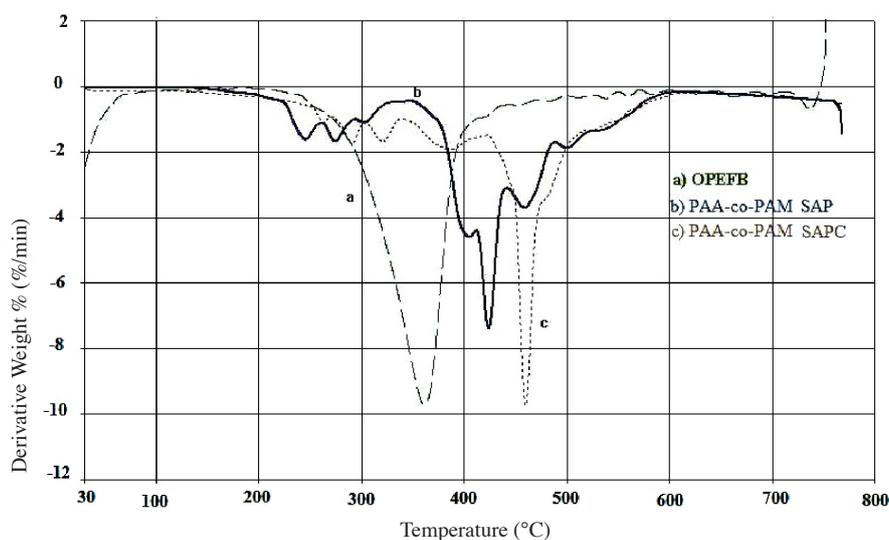


FIGURE 7. DTG curves of (a) OPEFB, (b) PAA-co-PAM SAP and (c) PAA-co-PAM SAPC

## CONCLUSION

In this work, OPEFB-g-PAA-co-PAM superabsorbent composite was prepared by graft copolymerization of AA and AM onto OPEFB backbones in the presence of a crosslinking agent. FTIR analysis indicated that AA, AM and OPEFB were incorporated in the superabsorbent composite. Swelling measurements of the synthesized superabsorbents in different salt solutions showed appreciable swelling capacity especially in sodium chloride solution. The thermal stability of the grafted OPEFB is better than that of the original fibre.

## ACKNOWLEDGEMENT

This research was supported by a grant from Ministry of Science, Technology and Innovation (MOSTI)-vot. No 78248.

## REFERENCES

- Abd El-Mohdy, H.L. & Abd El-Rehim, H.A. 2008. Radiation synthesis of kappa-carrageenan/acrylamide graft copolymers as superabsorbents and their possible applications. *Journal of Polymer Research* 16: 63-72.
- Buchholz, F. L. & Graham, A. T. 1998. *Modern Superabsorbent Polymer Technology*. New York: Wiley.
- Castel, D., Richard, A. & Audebert, R. 1990. Swelling of anionic and cationic starch based superabsorbent in water and saline solution. *Journal of Applied Polymer Science* 39: 11-29.
- Das, R.K., Basu, D. & Banerjee, A. 1999. Study of methyl-methacrylate-viscose fibre graft copolymerization and the effect of grafting on thermal properties. *Journal of Applied Polymer Science* 72: 135-140.
- Demitri, C., Del Sole, R., Scaleria, F., Sannino, A., Vasapollo, G., Maffezzoli, A., Ambrosio, L. & Nicolas, L. 2008. Novel superabsorbent cellulose-based hydrogels crosslinked with citric acid. *Journal of Applied Polymer Science* 110: 2453-2460.
- Fanta, G.F. Burr, R.C. & Doane, W.M. 1979. Graft polymerization of acrylamide and 2-acrylamido-2-methylpropane acid onto starch. *Journal of Applied Polymer Science* 24: 2015-2023.
- Ibrahim, S.M., El Salmawi, K.M. & Zahran, A.H. 2007. Synthesis of crosslinked superabsorbent carboxymethyl cellulose/acrylamide hydrogels through electron-beam irradiation. *Journal of Applied Polymer Science* 104: 2003-2008.
- Marandi, G.B., Esfandiari, K., Biranvand, F., Babapour, M., Sadeh, S. & Mahdavinia, G.R. 2008. pH sensitivity and swelling behavior of partially hydrolyzed formaldehyde-crosslinked poly(acrylamide) superabsorbent hydrogels. *Journal of Applied Polymer Science* 109: 1083-1092.
- Pourjavadi, A., Barzegar, Sh. & Mahdavinia, G.R. 2006. MBA crosslinked Na-Alg/CMC as a smart full-polysaccharide superabsorbent hydrogels. *Carbohydrate Polymers* 66: 386.
- Pourjavadi, A. & Ghasemzadeh, H. 2007. Carrageenan-g-poly(scrylamide)/poly(vinylsulfonic acid, sodium salt) as a novel semi-IPN hydrogel: Synthesis, characterization, and swelling behaviour. *Polymer Engineering Science* 47: 1388-1395.
- Pourjavadi, A., Ghasemzadeh, H. & Soleyman, R. 2007. Synthesis, characterization, and swelling behaviour of alginate-g-poly(sodium acrylate)/kaolin superabsorbent hydrogel composites. *Journal of Applied Polymer Science* 105: 2631-2639.
- Pourjavadi, A., Kurdtabar, M., Mahdavinia, G.R. & Hosseinzadeh, H. 2006. Synthesis and super-swelling behaviour of a novel protein based superabsorbent hydrogel. *Polymer Bulletin* 57: 813-824.
- Ramazani-Harandi, M.J., Zohuriaan-Mehr, M.J., Yousefi, A.A., Ershad-Langroudi, A. & Kabiri, K. 2006. Rheological determination of the swollen gel strength of superabsorbent polymer hydrogels. *Polymer Testing* 25: 470-474.
- Weaver, M.O., Montgomery, R.R., Miller, L.D., Sohns, V.E., Fanta, G.F. & Doane, W.M. 1977. A practical process for the preparation of super slurper, a starch based polymer with a large capacity to absorb water. *Die Starke* 29: 410-413.

Department of Polymer Engineering  
Faculty of Chemical Engineering  
Universiti Teknologi Malaysia  
81310 Skudai  
Johor Darul Takzim, Malaysia

\*Corresponding author; email: shahrir@cheme.utm.my

Received: 23 October 2009

Accepted: 5 August 2010