

## SYNTHESIS OF CASSAVA WASTE PULP-ACRYLAMIDE SUPER ABSORBENT: EFFECT OF INITIATOR AND CROSS-LINKER CONCENTRATION

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### ABSTRACT

Cassava waste pulp (CWP) contains high carbohydrates that can be modified into super absorbent polymer (SAP) through grafting and cross-linking copolymerization. Acrylamide (AM) was grafted onto CWP with ammonium persulfate (APS) as the initiator and N,N'-methylene-bis-acrylamide (MBA) as the cross-linker under atmospheric nitrogen. The effect of APS and MBA concentrations on water absorption capacity of saponified SAP was studied, while the evaluation of grafting ratio (GR) and grafting efficiency (GRE) was conducted on unsaponified SAP. The grafting success was indicated by the occurrence of IR peaks at wave numbers of 573, 765, 858, and 1667  $\text{cm}^{-1}$ . In the saponified SAP, the very intense characteristic band at 1562  $\text{cm}^{-1}$  is due to C=O asymmetric stretching in the carboxylate anion. Saponification increases significantly water absorption capacity compared to that of unsaponified SAP (from 39.79 g/g to 578.23 g/g). The highest water absorption capacity is reached at 0.74% APS and 0.09% MBA. The percentage of GRE and GR tends to increase with increasing APS concentration until reaching the highest value and then decreases. Effect of MBA concentration on water absorption capacity, GR, and on GRE is similar to the effect of initiator concentration on GR and GRE.

**Keywords:** super absorbent; cassava waste pulp; graft-copolymerization; acrylamide

### ABSTRAK

Onggok singkong merupakan hasil samping industri tapioka, mengandung karbohidrat tinggi yang dapat dimodifikasi menjadi polimer super absorben (SAP) melalui kopolimerisasi cangkok dan taut-silang. Akrilamida (AM) dicangkokkan ke onggok dengan inisiator amonium persulfat (APS) dan peanut-siang N,N'-methylene-bis-akrilamida (MBA) dalam suasana atmosfer nitrogen. Pengaruh konsentrasi APS dan MBA terhadap kapasitas penyerapan air dari SAP tersaponifikasi dipelajari, sedangkan nisbah (GR) dan efisiensi pencangkokan (GRE) dikaji hanya pada SAP tidak tersaponifikasi. Keberhasilan pencangkokan ditandai dengan munculnya pita serapan IR pada bilangan gelombang 573, 765, 858, dan 1667  $\text{cm}^{-1}$ . Dalam SAP tersaponifikasi, karakteristik pita yang kuat pada 1562  $\text{cm}^{-1}$  menunjukkan regangan asimetrik gugus C=O dari anion karboksilat. Saponifikasi meningkatkan kapasitas penyerapan air secara signifikan dibandingkan dengan SAP tidak tersaponifikasi (dari 39,79 g/g ke 578,23 g/g). Kapasitas penyerapan air tertinggi ini dicapai pada kondisi sintesis dengan APS 0,74% dan 0,09% MBA. Persentase GRE dan GR cenderung meningkat dengan bertambahnya konsentrasi APS sampai mencapai nilai tertinggi dan kemudian menurun. Pengaruh konsentrasi MBA pada kapasitas penyerapan air, GR, dan GRE mirip dengan pengaruh konsentrasi inisiator pada GR dan GRE.

**Kata Kunci:** super absorben; onggok singkong; kopolimerisasi cangkok; akrilamida

### INTRODUCTION

The acreage of cassava in 2011 was more than 1.18 million hectares with productivity 203.02 Qu/Ha and production close to 240 million tons [1]. On the processing of cassava root into flour, the residual pulp is occurred, that called cassava waste pulp. Until recently, there are no domestic and international documents that

indicate research interests on the potential of cassava waste pulp as super absorbent.

Cassava waste pulp (CWP) has relatively high carbohydrate content; starch is about 50-60% w/w [2], 61.84-69.90% [3] and 10.61-14.35% crude fibre [3]. As due to their hydroxyl content, a lot of work has been done to modify starch and cellulose, one of which is to modify into a super absorbent. Super absorbent polymer (SAP) have hydrophilic group that are able to

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**Table 1.** Variation of APS and MBA concentrations with 3 g CWP and 27 g acrylamide

No	Sample	APS (%)*	MBA (%)*
1	A1M1	0.74	0.06
2	A1M2	0.74	0.09
3	A1M3	0.74	0.13
4	A2M1	0.93	0.06
5	A2M2	0.93	0.09
6	A2M3	0.93	0.13
7	A3M1	1.11	0.06
8	A3M2	1.11	0.09
9	A3M3	1.11	0.13

\*percentage to the weight of acrylamide

absorb and retain fluids, and releasing it afterwards under certain conditions [4]. In general, SAP is synthesized by grafting or grafting-cross-linking copolymerization. Monomers used in grafting copolymerization are acrylic acid and acrylamide [5-6], and as cross-linkers are N,N-methylene bis-acrylamide (MBA), trimethylpropane triacrylate, and 1,4-butadienol dimethacrylate [7]. Initiators commonly used are persulfate, hydrogen peroxide [8], and cerium sulfate [9].

Grafting copolymerization has been done to modify cassava starch into SAP [10-11]. In addition to starch, lignocelluloses and its derivative are also used as substrate for graft copolymerization [12]. Mixture of acrylamide (AAM) and acrylic acid (AA) monomers were grafted on germinated gelatinized wheat starch using potassium persulfate (KPS) as an initiator to yield super absorbent [6]. The SAP produced by grafting-crosslinking process is expected to have a high water absorption capacity and release the water slowly. The aim of this study is to assess the effect of the initiator and cross-linker concentrations on water absorption capacity, grafting efficiency and grafting ratio of SAP obtained.

## EXPERIMENTAL SECTION

### Materials

Cassava waste pulp (CWP) was obtained from cassava home factory at Bogor, Indonesia. Nitrogen gas, HP was purchased from BOC Gases vendor, Indonesia. Acrylamide, ammonium persulfate (APS) and methanol, ethanol 96%, acetone, NaOH, HCl, and KBr for IR are all analytical grades and Manufactured by Merck (Darmstadt, Germany). N,N-Methylene bis-acrylamide (MBA) was manufactured by Fluka (Buchs, Switzerland).

### Instrumentation

FTIR spectra were taken on Shimadzu FTIR-Prestige-21 and surface morphology of SAP was

characterized using Ion Sputter JFC-1100 SEM instrument (JEOL).

### Procedure

#### Synthesis of super absorbent polymer

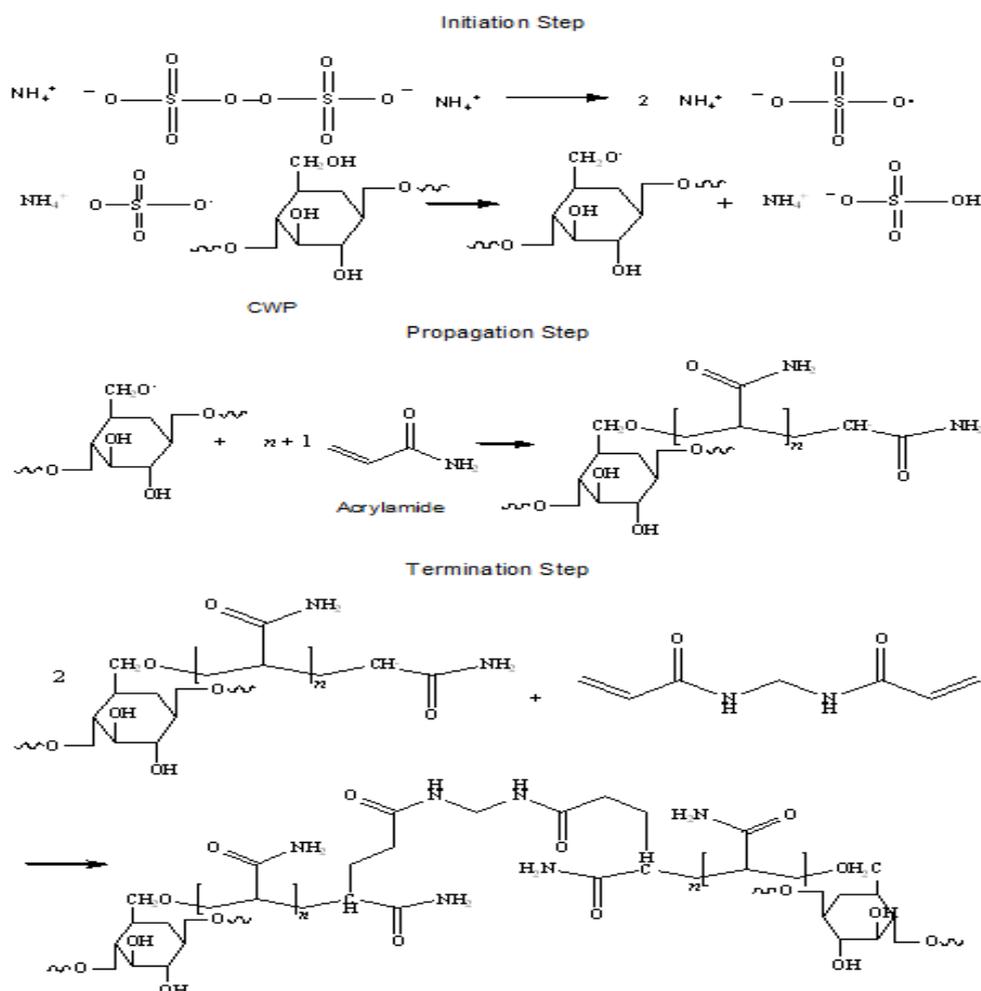
A series of super absorbent with different amounts of initiator and cross-linker were prepared by the following procedure: a 3 g of cassava waste pulp powder (100 mesh) and 150 mL distilled water were put in a 250-mL four-necked flask equipped with a stirrer, a condenser, a thermometer and a nitrogen line. The slurry was heated to 95 °C for 30 min under nitrogen atmosphere. A weight quantity of initiator APS (15-35 mg) was then added when the temperature reached 60–65 °C. After 15 min, 27 g of AAm and cross-linker MBA (200-300 mg) mixture solution was added. The water bath was heated slowly to 70 °C and kept for 3 h. Then the resulting product was washed several times with distilled water and ethanol and then dried at 70 °C to a constant weight. The dried product was milled and screened. All samples used had a particle size in the range of 60–80 mesh. The effect of APS and MBA were studied through factorial design (2 factors x 3 levels). Table 1 shows variations of the concentration of APS and MBA with the same concentration of monomer.

#### Saponification

Saponification was conducted as follow: 40 g of the graft copolymer was transferred to a flask containing 100 mL of 0.1 M NaOH solution and 100 mL of distilled water and the content was saponified at 90 °C for 2 h. The final concentration of the graft copolymer in NaOH solution was 16.67% (w/w) of the total mass, i.e., 40 g of the graft copolymer in 240 g of the mixture. The pH of the saponified products was then adjusted to 7 by the addition of a 0.1 M HCl solution and the saponified copolymer was coagulated and precipitated by the rapid addition of an excess amount of methanol. The precipitate was separated with filtration and washed thoroughly to remove the un-grafted starch, homopolymers as well as the un-reacted monomer. The thoroughly washed products were then dried in a vacuum oven at 60 °C until the weight of the polymer was constant. They were then ground and sized through an 80-mesh screen to leave the powdery SAP.

#### Water absorption capacity (Qeq)

The powdery SAP (0.1 g) was immersed in distilled water (200 mL) for 24 h at ambient temperature (25–30 °C) to reach an equilibrium swelling. The residual water was removed by filtration through a 100-mesh stainless steel screen with the water



**Scheme 1.** Proposed mechanistic pathway for synthesis of the CWP-based super absorbent

absorbed polymer left on the screen for at least 1 h to drain off the additional unabsorbed water. During this period, the screen was gently shaken to ensure that most of the un-absorbed water was separated. The water absorption was determined by weighing the swollen graft copolymer and its dried polymer in Eq. (1).

### Characterization

The graft ratio (GR, %) and graft reaction efficiency (GRE, %) was calculated from the nitrogen content using Eq. (2). The IR spectra of the super absorbent were recorded on a FTIR using KBr pellets. SEM studies were carried out on Ion SEM instrument after coating the sample with gold film using an acceleration voltage of 20 kV.

$$Q_{eq} = \frac{m_2 - m_1}{m_1} \quad (1)$$

$m_1$  = weight of dried sample (g)

$m_2$  = weight of swollen sample (g)

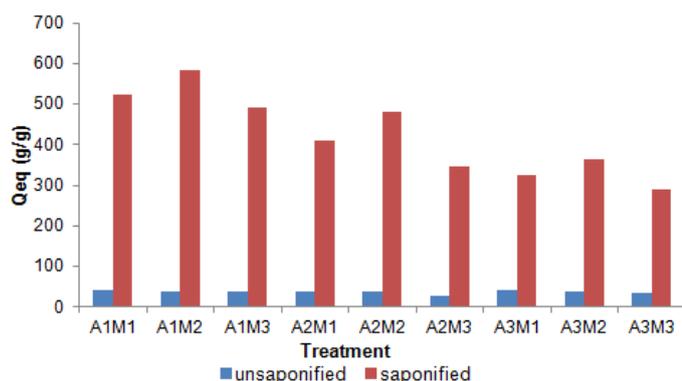
$$GR (\%) = \frac{100 \left[ N(\%) \times \frac{MW \text{ Acrylamide}}{Ar \text{ Nitrogen}} \right]}{100 - \left[ N(\%) \times \frac{MW \text{ Acrylamide}}{Ar \text{ Nitrogen}} \right]}$$

$$GRE (\%) = \frac{GR (\%)}{\% \text{ of monomer based on weight of CWP}} \times 100 \quad (2)$$

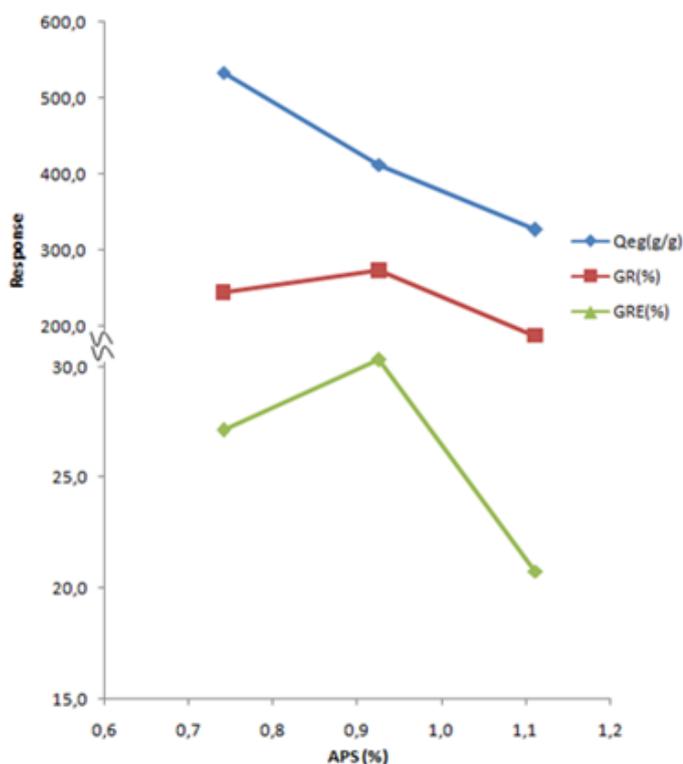
## RESULT AND DISCUSSION

### Synthesis of Super Absorbent Polymer CWP-g-AAm

Synthesis of SAP CWP-g-AAm was conducted through grafting copolymerization using APS as initiator and MBA as cross-linker under atmospheric nitrogen. Referring to [13] suggestion, it seems that the reaction mechanism for CWP-based super absorbent formation as is shown by Scheme 1. At the first step, the thermally dissociating initiator produce sulfate anion-radical. Then, the anion-radical abstracts hydrogen from



**Fig 1.** Effect of saponification on water absorption capacity



**Fig 2.** Effect of initiator concentration on water absorption capacity, GR and GRE

hydroxyl groups of CWP to form corresponding radicals. So, these macro radicals initiated monomers (acrylamide) grafted onto CWP backbones led to a graft copolymer. In addition, cross-linking reaction was carried out in the presence of a cross-linker, i.e., MBA, so that a three dimensional polymers network was obtained.

### Saponification

Saponification increase water absorption capacity of SAP [6,14]. All nine saponified obtained SAP increased their water absorption capacity compare to

those of unsaponified ones, with maximum indicated by sample Qeq (Fig. 1). The increase of Qeq value of saponified SAP is closely related to the conversion degree of amides ( $-\text{CONH}_2$ ) into carboxylic anions ( $-\text{COO}^-$ ) [6].

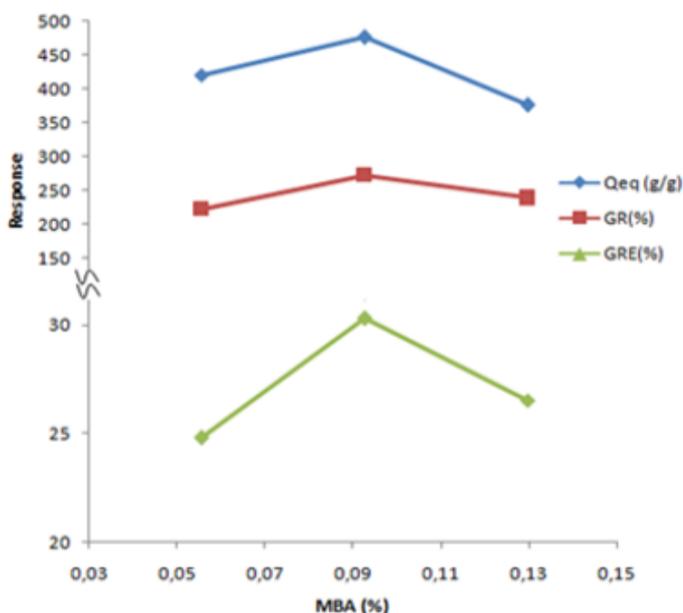
### Effect of Initiator Concentration on Water Absorption Capacity

The extent of radical polymerization depends on the type and concentration of the initiator. The effect of initiator concentration on water absorption is indicated by the SAP with following APS concentration i.e. 0.7, 0.9, and 1.1% (Fig. 2). Water absorption decreases with increasing initiator concentration. The highest water absorption capacity (582.87 g/g) was obtained at a concentration of 0.7% APS initiator. The result are in line with [15], that the initiator concentration increases would lead to the decrease of kinetic chain length, and will directly influence the molecular weight polymers, because more copolymer chains stop reacting.

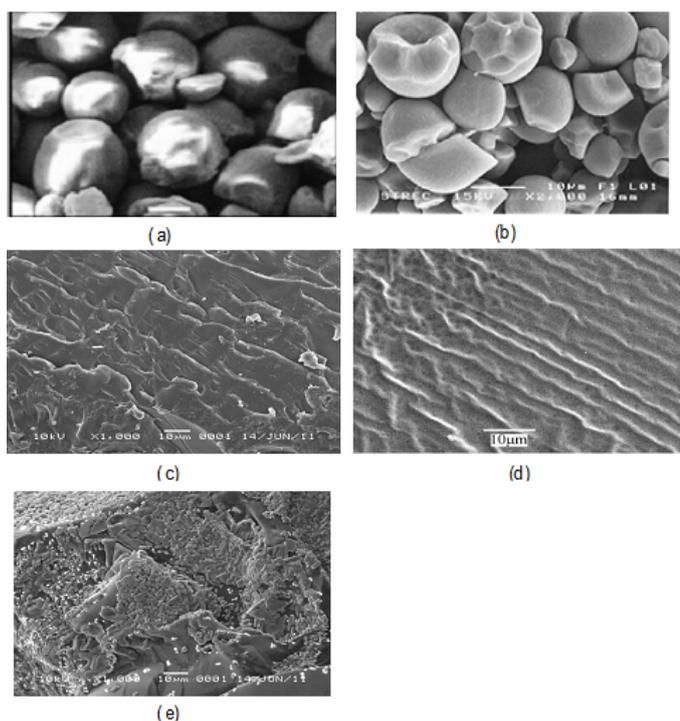
In expression of the percentage of grafting efficiency and grafting ratio tended to increase with increasing the concentration of initiator, reached a higher value and then decreased (Fig. 2). Free radicals were generated from the thermal decomposition of APS in various polymerization reactions. An increase in the concentration of the initiator increases the probability of hydrogen abstraction from the CWP backbone, and chain transfer reaction of the copolymer chain with CWP prone to increase the graft yield. However, the excessive increase in the concentration of APS resulted in free radical species from the decomposition of APS to give the termination reaction with CWP radicals or the growing polymer chain or a combination reaction between them, causing the grafting yield decreased.

### Effect of Cross-linker Weight on Water Absorption Capacity

Cross-linker in the synthesis of SAP serves to form three-dimensional polymer network. Water absorption capacity, percentage of grafting efficiency, and grafting ratio increase but at certain point those three properties decrease against concentration levels of MBA (Fig. 3). Those increases are caused by the bi-functionality of the cross-linker that reacted with polymer radicals of CWP substrate. While the decrease of the properties are may be due to the increase in the degree of cross-linking that resulted decreases in the size of the pores [16]. Therefore, increases in the degree of cross-linking will be inversely proportional to the water absorption capacity due to limiting space available for repulsion of the same charge [4]. The highest

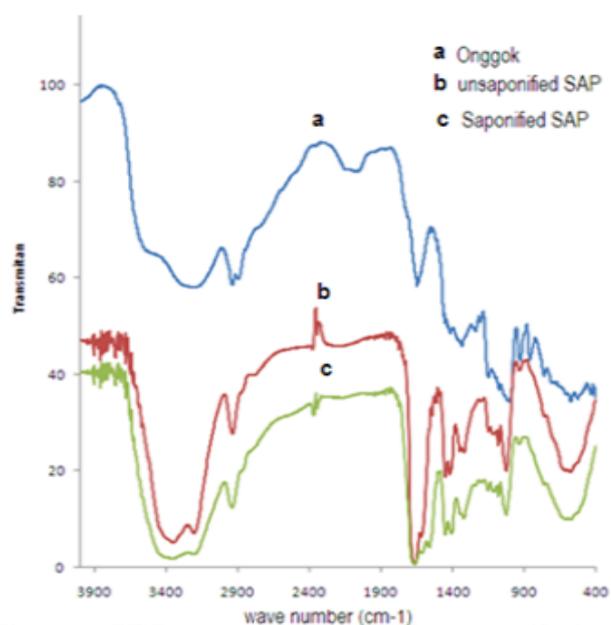


**Fig 3.** Effect of cross-linker concentration on water absorption capacity, GR and GRE



**Fig 5.** SEM photographs of (a) CWP, (b) starch [11], (c) unsaponified SAP CWP-g-AAm, (d) the starch-g-AAm/attapulgit [4], and (e) saponified SAP CWP-g-AAm

swelling was achieved at MBA concentration of 0.09%.



**Fig 4.** FTIR spectra of CWP, saponified and unsaponified SAP

#### Characterization of the Functional Groups of the Copolymers by FTIR

The synthesized copolymers were characterized by the functional groups using FTIR technique. The FTIR spectra for starch, saponified and unsaponified CWP-g-AAm are presented in Fig. 4. The results show that the IR spectrum of CWP (Fig. 4a) display the O–H stretching absorption in the region of 3550–3200  $\text{cm}^{-1}$ , the C–H stretching at 2930  $\text{cm}^{-1}$ , and the wave numbers of 1158, 1081, and 1015  $\text{cm}^{-1}$  for the C–O–C stretching (a triplet peak of starch). The peaks at 3400, 3200, 1650, and 1600  $\text{cm}^{-1}$  of unsaponified SAP attributed the O–H stretching, N–H stretching, the C=O stretching and N–H bending of the amide bands, respectively, which are characteristics of the  $-\text{CONH}_2$  group of acrylamide (Fig. 4b). In addition, the peak at 1411  $\text{cm}^{-1}$  and the weak band at 765–710  $\text{cm}^{-1}$  are attributed by  $-\text{C}-\text{N}$  stretching and the N–H out of plane bending, respectively, which are typical absorption bands of the amide group. Under saponification conditions, the amide groups were converted to carboxylate anions, as indicated by intense band at 1562  $\text{cm}^{-1}$  that due to C=O asymmetric stretching in the carboxylate anion (Fig. 4c).

#### Surface Morphology of the Super Absorbent Copolymer

The SEM photographs of CWP, saponified and unsaponified SAP are illustrated in Fig. 5. SEM of CWP shows that it contains starch granules (Fig. 5a) similar

to SEM photograph of [11] (Fig. 5b). Starch granules have an irregular shape and varied particle sizes with smooth surface while the graft copolymers have a different surface morphology. The SEM photographs of the unsaponified CWP-g-AAm in Fig. 5c exhibits a smooth and dense surface similar to that of the Zhang's SEM photograph on starch-g-AAm/atapulgit (Fig. 5d). While saponified CWP-g-AAm shows a relatively coarse and undulant surfaces (Fig. 5e). Also, some pores can be observed in the surface of saponified CWP-g-AAm. Coarse, undulant and pores seem to be related to its water absorption capacity. Therefore, water absorption capacity of saponified is higher than that unsaponified SAP.

## CONCLUSION

Saponification increases water absorption capacity significantly compared to that of unsaponified SAP. The highest water absorption capacity is reached at 0.7% APS and 0.09% MBA (from 39.79 g/g to 578.23 g/g). The IR spectrum of CWP-g-AAm gives the characteristic absorption peaks of the COONH<sub>2</sub> that confirm the occurrence of grafting and cross-linking. SAP CWP-g-AAm and its saponified SAP reveal different surface morphology.

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## REFERENCES

1. Anonymous, Badan Pusat Statistik (BPS), 2011, [http://www.bps.go.id/tnmn\\_pgn.php?kat=3](http://www.bps.go.id/tnmn_pgn.php?kat=3), access July 10, 2011.
2. Ubalua, A.U., 2007, *African J. Biotechnol.*, 6, 18, 2065–2073
3. Srinorakutara, T., Kaewvimol, L., and Saengow, L., 2006, *J. Sci. Res. Chula. Univ.*, 31, 1, 77–84.
4. Zhang, J., Li, A., and Wang, A., 2006, *Carbohydr. Polym.*, 65, 2, 150–158.
5. Li, A., Zhang, J.P., and Wang, A.Q., 2007, *Bioresour. Technol.*, 98, 2, 327–332.
6. Teli, M.D., and Waghmare, N.G., 2009, *Carbohydr. Polym.*, 78, 3, 492–496.
7. Swantomo, D., Megasari, K., and Saptaaji, R., 2008, *Jurnal Forum Nuklir*, 2, 143–156.
8. Moad, G., and Solomon, D.H., *The Chemistry of Radical Polymerization*, 2<sup>nd</sup> ed., Elsevier Inc., San Diego, CA, 2006, p. 639.
9. Al, E., Güçlü, G., İyim, T.B., Emik, S., and Özgümüş, S., 2008, *J. Appl. Polym. Sci.*, 109, 1, 16–22.
10. Khalil, M.I., and Farag, S., 1998, *J. Appl. Polym. Sci.*, 69, 1, 45–50.
11. Lanthong, P., Nuisin, R., and Kiatkamjornwong, S., 2006, *Carbohydr. Polym.*, 66, 1, 229–245.
12. Hon, D.N-S, 1982, Graft Copolymerization of Lignocellulosic Fibers, *ACS Sym. Ser.*, 187, DOI: 10.1021/bk-1982-0187.
13. Pourjavadi, A., and Mahdavinia, G.R., 2006, *Turk. J. Chem.*, 30, 595–608.
14. Kiatkamjornwong, S., 2007, *Sci. Asia.*, 33, 39–43.
15. Liu, J., Wang, Q., and Wang, A., 2007, *Carbohydr. Polym.*, 70, 2, 166–173.
16. Chauhan, G.S., and Lal, H., 2003, *Desalination*, 159, 2, 131–138.