

## CHAPTER 5

### CONCLUSION and SUGGESTION

#### 5.1 Conclusion

High-water absorption polymers of the saponified starch-*g*-polyacrylamide, saponified starch-*g*-poly(acrylic acid), and saponified starch-*g*-poly(acrylamide-*co*-acrylic acid) were synthesized by a simultaneous irradiation technique using gamma-rays as the initiator under various conditions followed by alkaline saponification. The absorption behavior of high-water absorption polymers is related to their chemical structure, chemical composition, the absorbing environment, and the nature of the solution. The results are summarized as follows:

1. Starch-*g*-polyacrylamide, starch-*g*-poly(acrylic acid), and starch-*g*-poly(acrylamide-*co*-acrylic acid) were synthesized and confirmed by the FT-IR spectroscopy. The infrared absorption spectra of starch-*g*-polyacrylamide give the absorption peaks of the cassava starch and the absorption peaks of -CONH<sub>2</sub> group containing in the acrylamide. When the starch-*g*-polyacrylamide was saponified carefully, no addition peaks can be significantly observed. It indicates that only a minute amount of the carboxamide groups in the acrylamide moiety can be converted into the carboxylate groups. In the case of starch-*g*-poly(acrylic acid), its infrared absorption spectra give absorption peaks of cassava starch and give the additional peaks of the -COOH group containing in the acrylic acid. After starch-*g*-poly(acrylic acid) has been saponified, the disappearance of the absorption peaks of the -COOH

group and the appearance of the absorption peaks of the -COOK group indicates that the carboxylic group of the acrylic acid moiety has been converted to the carboxylate group. The IR spectra of starch-*g*-poly(acrylamide-*co*-acrylic acid) gives absorption peaks of cassava starch, acrylamide, and acrylic acid, and after saponification of this graft copolymer, one can observe absorption peaks of the carboxylate group of the acrylate in stead of the carboxylic group of acrylic acid.

2. The optimum time for a saponification of the graft copolymer with 5% potassium hydroxide solution at room temperature is thirty minutes. During this period all acrylic acid moieties can be converted to the acrylate salt and the insignificant amount of the acrylamide moiety can be converted into the acrylate salt.

3. Increasing the monomer-to-starch ratio at a fixed acrylamide-to-acrylic acid ratio 50:50 enhances the grafting efficiency, the percentage add-on, and the grafting ratio. The water absorption is highest at the monomer-to-starch ratio of 2:1 (755 times its original dried weight) and decreases with the increasing monomer-to-starch ratio higher than 2:1. This may be due to that chain transfer to polymer increases with increasing monomer concentration, which results in increasing amounts of branching and self-crosslinking reactions. Increasing crosslinking density restricts the swelling of the highly water absorbents by elastic retraction forces.

4. Increasing the quantities of total dose to graft copolymerization of acrylamide, or acrylic acid onto the starch at the fixed three dose rates will not only decrease the homopolymer but also increase the grafting efficiency, percentage add-on, and grafting ratio. However, the total dose higher than 6.0 kGy at the dose rate of 2.24 and 5.75 kGy hr<sup>-1</sup> in the case of grafting acrylamide onto starch; and at 14.75 kGy hr<sup>-1</sup>

in the case of grafting acrylic acid onto starch, the grafting efficiency unfortunately decreases. This is attributed to the formation of small fragments of  $\text{OH}^\cdot$ , and  $e_{\text{aq}}^-$  to form homopolymer at the expense of grafting. The highest water absorption is obtained at the total dose of 6.0 kGy and dose rate of 2.24 kGy  $\text{hr}^{-1}$ .

5. An increase in the irradiation dose rate at the fixed total dose decreases conversion of the monomer, grafting efficiency, percentage add-on, grafting ratio, and water absorption due to the surplus radicals and short kinetic chains tend to terminate the grafting growing chains before an adequate grafting is reached.

6. Adding nitric acid into the reaction mixture of starch and acrylamide before irradiation, graft copolymerization increases along with the grafting efficiency, percentage add-on, and grafting ratio; because an increase in hydrogen atom yields  $[\text{G}(\text{H})]$  from secondary electron capture by  $\text{H}^+$  which leads to the increasing the number of grafting sites, followed by increasing grafting probability caused by the partitioning phenomena. Unfortunately, the water absorption decreases because of the imidization of the amide pendants in the copolymer. The imidized structure of starch grafted acrylamide restricts its swelling due to more rigidity of the chains.

7. When the maleic acid was added into the mixture of starch and acrylamide, the homopolymer increases while the grafting efficiency, percentage add-on, and grafting ratio decreases. It indicates that both monomers prefer to copolymerize as the free, ungrafted copolymer rather than the grafted copolymer onto starch, the water absorption thus decreases.

8. Adding nitric acid into the reaction mixture of starch and acrylic acid before irradiation decreases the conversion of monomer, grafting efficiency, percentage add-on, and grafting ratio. Nitric acid hydrolyzes starch backbone before the starch can be grafted with acrylic acid. Fortunately, adding the nitric acid into the starch-acrylic acid mixture increases water absorption.

9. Increasing the concentration of nitric acid added into the reaction mixture of starch, acrylamide and acrylic acid before irradiation, graft copolymerization decreases in terms of the conversion of monomer, grafting efficiency, percentage add-on, grafting ratio, and water absorption. At higher acidity of nitric acid, it could attack and hydrolyze the starch backbone before the sufficient grafting occur.

10. The optimum weight ratio of acrylamide-to-acrylic acid used in graft copolymerization is in the range between 70:30 and 50:50. At this range, the grafted copolymer of starch obtained has a high grafting efficiency, which gives the saponified graft copolymer with a high water absorption.

11. The swelling of the copolymer which retains distilled water as high as 1142 g g<sup>-1</sup> its dried weight, was studied in the isotonic fluid of 0.9% w v<sup>-1</sup> of NaCl, MgCl<sub>2</sub>, and CaCl<sub>2</sub> solutions. The water absorption in the salt solutions is very much lower than that in distilled water due to the screening of the ionic charges bound to the network and to the decrease of the osmotic pressure difference between inside of the gel and the external solution. The water absorption in the multivalent saline solution decreases much more strongly in comparison with that in the monovalent saline solution.

12. The water absorbency of the copolymer was found to increase with increasing pHs of the external solution until pH 5, after which it remains relatively unchanged because of the anionic nature of copolymer.

13. The surface morphology of the saponified graft copolymers and grafting polymers studied by SEM reveal that saponified graft copolymers having the higher absorbency are more porous, whereas the grafted polymers are composed of irregularly crosslinked polymer due to the formation of imide structure during the acid hydrolysis reaction of starch.

## **5.2 Suggestion and Future Work**

The synthesis of saponified cassava starch-acrylamide/acrylic acid graft copolymers as superabsorbent polymers by a simultaneous irradiation technique should be further studied as follows:

1. Investigation of the graft copolymerization at the dose rate lower than 2.24 kGy hr<sup>-1</sup>. Based on the present work, the irradiation at the lower dose rate, the graft copolymer so obtained has a higher grafting yield and also gives the saponified graft copolymer with a higher water absorption. We anticipate that the dose rate lower than the one used in this work may/may not produce a better starch grafted AM/AA absorbents.

2. The effect of other kinds of mineral acid additive, such as sulfuric acid, and hydrochloric acid at various concentrations on grafting reaction and water absorption

should be persuaded. These acids may be better in activating the trunk polymer of starch by the hydrogen abstraction reaction.

3. The effect of other kinds of diprotic acid, such as itaconic acid at various concentrations on grafting reaction and water absorption capacity should be carried out.

4. The effect of particle size of saponified graft copolymer on the water absorption is worthwhile to investigate.

5. The gel strength of the saponified graft copolymers and improvement of their gel strength using a very mild crosslinking agent such as *N,N'*-methylenebisacrylamide are recommended to carry out.