

## CHAPTER V

### CONCLUSION and SUGGESTION

The investigation on the chemical modification of native cassava starch by a graft copolymerization has led to a new type of polymer with attractive water absorption properties. This material is a biodegradable high-water absorbing polymer. The results obtained are very significant in terms of the numerous applications possible. This type of product had already been used in agricultural, horticultural, silviculture areas and in industrial goods such as sanitary napkins, baby diapers, etc. The results in this experiment match well similar materials, synthesized from different sources of substrate by the other methods, in industrial countries. The initiator system used in this experiment is the hydrogen peroxide-ascorbic acid system. The advantages of this system are that it is cheap, the residual monomer is less toxic than the others, and there is no residual initiator at all in the final product. However, this type of graft copolymerization imposes only a high viscosity problem due to the Trommsdorf effect on graft copolymerization and the additional effect of the high molecular weight more than  $10^6$ , of the trunk polymeric substrate of cassava starch.

## 5.1 Conclusion

From all the experiments, the results can be concluded as the following:

5.1.1 Cassava starch-g-PAA copolymer was synthesized and confirmed by the FT-IR infrared spectrophotometry. Obviously, the several characteristic peaks observed in the FT-IR spectrum of the saponified starch-g-PAA copolymer indicate the occurrence of the graft copolymerization of AA onto cassava starch in which the absorption peaks of the C=O stretching occur at  $1,709\text{ cm}^{-1}$  and the C=O and C-O asymmetry and symmetry stretching of carboxylate anions occur at  $1,566$  and  $1,408\text{ cm}^{-1}$ , respectively. The latter two peaks indicate that PAA grafts are converted into their inorganic salt (potassium polyacrylate) when the copolymer is saponified. The carboxylate group is capable of water absorption properties based on the differential in osmotic pressure due to the potassium carboxylate semipermeable membrane.

5.1.2 The approximate molecular weights of the graft PAA calculated by the extrapolation of calibration curve to the retention time range are in the range of 2,917-4,294 and 4,294-15,664 for the starch-g-PAA copolymer synthesized by 2.95 M of AA, 0.2217 M  $[\text{H}_2\text{O}_2]$  with a reaction temperature of  $35^\circ\text{C}$ . The degrees of polymerization of the graft PAA are in the range of 40-218. The molecular weight is relatively

low compared with the others in the literature reviewed in Chapter 2. This result can probably be due to the small amount of monomer concentration to be grafted on the starch substrate.

5.1.3 The effect of the starch/acrylic acid ratio on water absorption of the saponified starch-g-PAA copolymers in deionized distilled water was that the acrylic acid content increased from 1.47 M to 2.95 M, the water absorption increases gradually. An increase in AA concentration higher than 2.95 M, reduced the water absorption most probably due to an increase in the number of the PAA homopolymer. The maximum water absorption is 234 g/g while the minimum water absorption is 24 g/g.

5.1.4 The effect of the hydrogen peroxide concentration on the water absorption of the saponified starch-g-PAA copolymers in deionized distilled water was that the  $H_2O_2$  concentration increased from 0.0553 M to 0.2217 M, the water absorption increased. An increase in  $H_2O_2$  high than 0.2217 M reduces the water absorption probably due to an increase in grafting frequency. Under this range of  $H_2O_2$  concentration, the maximum water absorption is 234 g/g while the minimum water absorption is 18 g/g.

The effect of the reaction temperature on the water absorption of the saponified starch-g-PAA copolymers in deionized distilled water was that the reaction tempera-

ture increased from 35 to 65°C, the water absorption decreased gradually. The maximum water absorption was 234 g/g while the minimum water absorption was 40 g/g. It is considered that the temperature effect was the most important one as the decomposition rate of  $H_2O_2$  is accelerated at a rate of 2.2 by a raise of 10°C. Oxygen is the by product which destroys the co-initiator and inhibits polymerization.

5.1.5 The effect of the starch/AA ratio on the water absorption capacity of the saponified starch-g-PAA copolymers in 0.1, 0.5, 1.0, and 2.0% w/v of NaCl solutions imposed the similar trend as that in the deionized distilled water. When the starch/AA ratio increased higher than 30:2.95, the water absorption decreased. The water absorption of the starch grafted copolymers by the 30:2.95 starch/AA ratio was maximum at 134, 105, 91, and 59 g/g respectively. The water absorption at 30:4.42 starch/AA ratio was minimum at 18, 13, 11, and 10 g/g respectively. An increase in ion content in water reduces the water absorption due to a decrease in the osmotic pressure difference between the external and the internal solutions of the starch grafted copolymer.

5.1.6 The effect of the hydrogen peroxide concentration on the water absorption capacity of the saponified starch-g-PAA copolymers in 0.1, 0.5, 1.0, and 2.0% w/v of

NaCl solutions imposed the similar trend as that in the deionized distilled water. When the  $H_2O_2$  concentration increased higher than 0.2217 M, the water absorption decreased gradually. The water absorption of the starch grafted copolymers by the 0.2217 M  $H_2O_2$  concentration was maximum at 134, 105, 91, and 59 g/g respectively. The water absorption at the 0.3322 M  $H_2O_2$  concentration was minimum approximately at 10-13 g/g.

The effect of the reaction temperature on the water absorption capacity of the saponified starch-g-PAA copolymers in 0.1, 0.5, 1.0, and 2.0% w/v of NaCl solutions imposed the similar trend as that in the deionized distilled water. When the reaction temperature increased, the water absorption decreased. The water absorption of the starch grafted copolymers reacted at 35°C was maximum at 134, 105, 91, and 59 g/g respectively. The water absorption at the starch grafted copolymer polymerized at 65°C was minimum at 22, 18, 15 and 15 g/g respectively.

An increase in ion content in water reduces the water absorption due to a decrease in the osmotic pressure difference between the external and the internal solutions of the starch grafted copolymer.

5.1.7 The effect of the starch/acrylic acid ratio on the water absorption capacity of the saponified starch-g-PAA copolymers in 0.1, 0.5, 1.0, and 2.0% w/v of  $MgCl_2$

solutions gave the similar trend as that in the deionized distilled water. When the starch/AA ratio increased higher than 30:2.95, the water absorption decreased. The water absorption of the starch grafted copolymers by the 30:2.95 starch/AA ratio was maximum at 56, 25, 20 and 19 g/g respectively. The water absorption at 30:4.42 starch/AA ratio was minimum at 13, 10, 9, and 8 g/g respectively.

5.1.8 The effect of the  $H_2O_2$  concentration on the water absorption capacity of the saponified starch-g-PAA copolymers in 0.1, 0.5, 1.0, and 2.0% w/v of  $MgCl_2$  solutions gave the similar trend as that in the deionized distilled water. When the  $H_2O_2$  concentration increased higher than 0.2217 M, the water absorption decreased. The water absorption of the starch grafted copolymers by the 0.2217 M  $H_2O_2$  concentration was maximum at 56, 25, 20, and 19 g/g respectively. The water absorption at the 0.3322 M  $H_2O_2$  concentration was minimum at 10, 9, 9, and 9 g/g respectively.

The effect of the reaction temperature on the water absorption capacity of the saponified starch-g-PAA copolymers in 0.1, 0.5, 1.0, and 2.0% w/v of  $MgCl_2$  solutions gave the similar trend as that in the deionized distilled water. When the reaction temperature increased, the water absorption decreased. The water absorption of the starch grafted copolymers reacted at  $35^\circ C$  was maximum at 56, 25, 20, and 19 g/g respectively. The water absorption

at the starch grafted copolymer polymerized at  $65^{\circ}\text{C}$  was minimum at 20, 17, 15, and 15 g/g respectively.

5.1.9 The effect of monovalent ( $\text{Na}^+$ ) and divalent ( $\text{Mg}^{+2}$ ) cations on the water absorption of the hydrolyzed starch-g-PAA copolymer in  $\text{NaCl}$  and  $\text{MgCl}_2$  solutions is summarized. At the same concentration,  $\text{MgCl}_2$  solutions impose a lower absorption value than those of  $\text{NaCl}$  solutions. The decrease of absorption is due to screening of the ionic charges bound to the starch grafted copolymer and to the decrease of the osmotic pressure difference between the copolymer and the external solution when the ionic strength increases (92).

The decrease of absorption in  $\text{MgCl}_2$  can be due to the complexing ability of the carboxylate groups inducing intramolecular and intermolecular complexes formation. Consequently, the crosslink density of the starch grafted copolymer increases.

5.1.10 The effect of the starch/acrylic acid ratio on the water absorption capacity of the saponified starch-g-PAA copolymers in  $\text{K}_3\text{PO}_4 \cdot 3\text{H}_2\text{O}$ ,  $\text{KCl}$ ,  $\text{NH}_4\text{Cl}$ , and  $(\text{NH}_4)_2\text{HPO}_4$  solutions at the same concentration of 0.9% w/w was maximum at 57, 63, 38, and 52 g/g respectively. These maximum values are obtained from the hydrolyzed starch-g-PAA copolymer synthesized with 2.95 M acrylic acid.

5.1.11 The effect of the hydrogen peroxide concentration on the water absorption capacity of the saponified starch-g-PAA copolymers in  $K_3PO_4 \cdot 3H_2O$ , KCl,  $NH_4Cl$ , and  $(NH_4)_2HPO_4$  solutions at the same concentration of 0.9% w/w was maximum at 57, 63, 38, and 52 g/g respectively. These maximum values are obtained from the hydrolyzed starch-g-PAA copolymer synthesized with 0.2217 M  $H_2O_2$ .

The effect of the reaction temperature on the water absorption capacity of the saponified starch-g-PAA copolymers in  $K_3PO_4 \cdot 3H_2O$ , KCl,  $NH_4Cl$ , and  $(NH_4)_2HPO_4$  solutions at the same concentration of 0.9% w/w was maximum at 57, 63, 38, and 52 g/g respectively. These maximum values are obtained from the hydrolyzed starch-g-PAA copolymer synthesized with the reaction temperature of 35°C.

5.1.12 Water retention capacity in sand was 0.3 g/g. Mixtures of sand with 0.5, 1.0, 2.0 and 3.0% of saponified starch-g-poly(acrylic acid) copolymers could increase water retention gradually up to a maximum value of 141 g/g at 3.0% of the saponified polymer synthesized from 2.95 M of acrylic acid, 0.2217 M  $H_2O_2$  concentration and the reaction temperature of 35°C.

## 5.2 Suggestion and Further Work

There are many techniques to synthesize a high-water absorbing polymer based on grafting vinyl monomers onto



starch. The current synthesis technique uses a hydrogen peroxide-ascorbic acid initiation method. To develop an even better and new high-water absorbing polymers to be used in agriculture and other applications, further work should be carried out as follows.

5.2.1 Pursue other suitable method to separate the polyacrylate graft chains from the polysaccharide backbone in order to determine the grafting parameters, grafting efficiency, grafting frequency, percentage of grafting, % add-on, and % homopolymer. These will give some inside information to regulate this type of material with a higher water absorption.

In this work, there is a problem of separating the acrylate graft chains from the polysaccharide backbone as described in Chapter 4. Further work perhaps should use the following method to cleave the acrylate graft chains from the polysaccharide backbone:

The periodate-methoxide method was described by Yang, S. and A. Liu (93). 4 g of the hydrolyzed starch-g-PAA copolymer was dispersed in 10 cm<sup>3</sup> H<sub>2</sub>O. Into the mixture was added 20 cm<sup>3</sup> of a 10% w/v NaIO<sub>4</sub> aqueous solution. The mixture was stirred in the dark for 3 days and then filtered. The solid product was washed with H<sub>2</sub>O to remove the salt and then was washed with methanol to remove H<sub>2</sub>O. 10 cm<sup>3</sup> methanol and 5 cm<sup>3</sup> of 1.2 M sodium methoxide were then added at 0°C. After stirring well and standing over-

night, add KOH to the mixture to change PAA to the product containing potassium salt, and the mixture was then precipitated with the suitable nonsolvent (such as methanol) of potassium polyacrylate in a proper cooling system.

5.2.2 Use other standards such as polysaccharide standards which give suitable molecular weights for this work and the suitable series of the Ultrahydrogel columns to determine molecular weights and their distribution of the polyacrylate graft chains.

5.2.3 Utmost efforts should be pursued to develop a technique for a more stable starch-based high-water absorbing polymer under severe conditions of daily applications such as very high temperature or pressure, a very dry atmosphere, a poisonous or toxic soil environment such as aluminum poisoning soil.

5.2.4 Instead of using acrylic acid as a grafting monomer, methacrylic acid and/or other unsaturated organic acids with an inherently stable structure and better thermal properties such as higher  $T_g$  and  $T_d$  could also be used.

5.2.5 Improve gel strength of the saponified grafted copolymer by using a very mild crosslinking agent such as N,N-bismethylene acylamide or diethylene glycol diacrylate.

5.2.6 Study the influence and extent of crosslinking density on the water absorption capacity.

The sections of 5.2.5 and 5.2.6 will increase the water absorption of the HSPAA superabsorbent when an optimum condition is attained. The roughly structural diagram of the molecules of the superabsorbent in terms of crosslinking density effects on its water absorption is present in Figure 5.1.

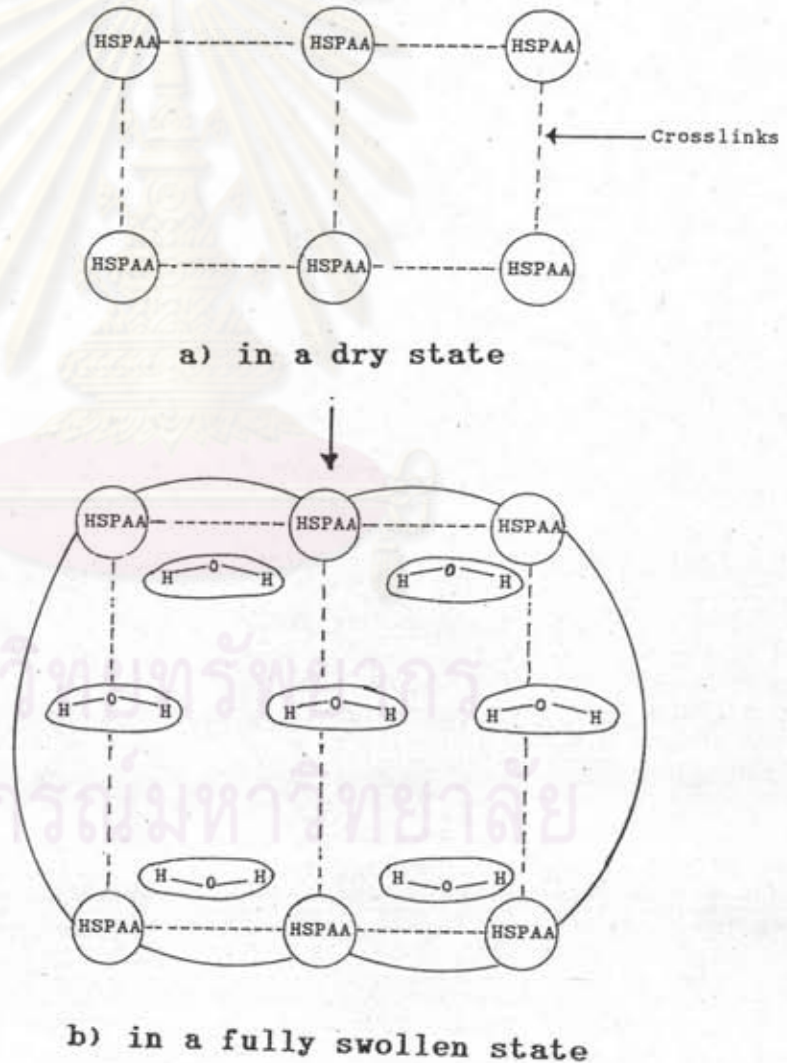


Figure 5.1 Structural diagram of the molecules of HSPAA in terms of crosslinking effects on its water absorption.