

CHAPTER V

CONCLUSION and SUGGESTION

The research on enhancement of radiation grafting copolymerization and water absorption of Cassava starch graft copolymer under the constant dose rate to various total doses, several attempts were used, based on theoretical considerations, to pursue the possible technologies to increase the grafting efficiency and water absorption. Both the positive and negative effects to the above mentioned purposes are found. The positive influences toward enhancement of the grafting reaction and water absorption are, of course, gratifying. The negative part of the result is the master for future improvement. However, both are presented as the following:

1. Cassava starch-g-PAN was synthesized and confirmed by the FT-IR spectroscopy. The nitrile stretching band appeared at $2,245\text{ cm}^{-1}$ during grafting and disappeared during saponification; the characteristic bands appeared at $3,400, 1082-1,160\text{ cm}^{-1}$ indicated the occurrence of grafting of Cassava starch. The disappearance of the nitrile group, on the other hand, resulted in the appearance of carboxylate and carboxamide groups. The carboxylate group $-\text{COOK}$ gave rise a strong asymmetrical stretching band at $1,572\text{ cm}^{-1}$, and the carboxamide group $-\text{CONH}_2$ gave a weak, symmetrical stretching band at $1,402\text{ cm}^{-1}$. The primary amide could not be detected, probably as a result of a relatively low concentration, and/or due to the usually low intensity of the NH stretching band and overlapping with existing ones, the OH stretching bands of the starting material (1). These two groups are capable

of water absorption properties based on the differential in osmotic pressure due to the potassium carboxylate and carboxamide semipermeable membrane.

2. By increasing the quantities of total dose, increases in percentage homopolymer and grafting frequency at the total dose other than 3.5 kGy were observed; likewise, the percent add-on, the percent grafting efficiency, the percent grafting ratio, and the water absorption value at the total dose other than 3.5 kGy was decreased. The viscosity average molecular weight (M_v) and the percent conversion of the monomer increased with increasing the total dose. Water absorption capacity of Cassava starch-g-PAN synthesized was in the range of 289 to 500 times their original dried weight depending upon the quantities of total dose, based on a 1:2 ratio of the starch(g) and AN(ml).

3. As a general rule of graft copolymerization, homopolymer formation usually accompanies grafting reaction at the expense of the graft copolymer. It is necessary to suppress the formation of homopolymer. The result indicated that the aluminium foil is the best metal suppressor for homopolymer formation. It produces the saponified starch-g-polyacrylonitrile with a water absorption value up to 500 times their original dried weight, based on the total dose of 3.5 kGy and a 1:2 ratio of the starch(g) and AN(ml). Aluminium foil releases electrons when it absorbs gamma rays. Electrons ejected do participate actively in the radiation grafting processes.

4. Increasing the MEHQ inhibitor content in the irradiated mixture, increases the percent homopolymer formed, while the percent grafting efficiency, the percent grafting ratio, the conversion of monomer, the percent add-on, the molecular weight average and the water absorption value, and the grafting frequency were decreased. The water absorption of saponified starch-g-polyacrylonitrile was in the range of 172 to 431 times upon the inhibitor

content, based on the total dose of 3.5 kGy and a 1:2 ratio of starch(g) and AN (ml). Since the inhibitor can disperse in aqueous phase more than monomer phase, the radicals in aqueous phase and starch are suppressed. The chance of monomer in grafting is reduced. This results in the decrease of water absorption while increasing the inhibitor content.

5. Adding nitric acid in the reaction solution before irradiation, decreased the percent homopolymer and the molecular weight average (M_v) of the grafted PAN, while the percent grafting efficiency, the percent grafting ratio, the percent add-on, the grafting frequency and the water absorption value increased at the total dose of 3.5 kGy and a 1:2 ratio of starch(g) and AN(ml). Because in the acid media, the radiolysis of water increases in the $G(H^\bullet)$ that leads to increased grafting sites on the starch backbone by hydrogen abstraction reactions. Thus, grafting reaction is enhanced. The water absorption of saponified starch-g-polyacrylonitrile produced with the nitric acid medium was 550 times their original dried weight while that of saponified starch-g-polyacrylonitrile produced in neutral medium was 500 times their original dried weight.

6. Adding the styrene as comonomer in the irradiated mixture, increased the percent homopolymer of both styrene and acrylonitrile, while the water absorption decreased when total dose used was in the range of 3.5 to 10 kGy at the 1:4 ratio of styrene(ml) and acrylonitrile(ml). The water absorption capacity of saponified starch-g-polyacrylonitrile was in the range of 443 to 319 times their original dried weight. Because the grafted chains have both styrene and acrylonitrile molecules, the carboxylate groups that are derived from the hydrolysis of acrylonitrile with potassium hydroxide solution is low. This brings about decrease in the water absorption.

7. By increasing the acrylonitrile content, increases in the percent homopolymer formed, the percent add-on, the grafting ratio, and the molecular weight (M_v) of the grafted PAN are observed. As the AN content increased, there were more probability that AN could be grafted on the starch backbone and converted to homopolymer. The grafting frequency was in the range of 1,033 to 1,133 AGUs/chain. The water absorption value of saponified starch-g-polyacrylonitrile was in the range of 237 to 550 times their original dried weight depending on the AN content from 10 ml to 25 ml based on 10 g of Cassava starch substrate in the nitric acid medium. The reactions were carried out with the total irradiation dose of 3.5 kGy. The starch/acrylonitrile ratio of 10:20 is an attractive figure because it gives the HSPAN with the highest water absorption value of 550.

8. Water absorption capacity of the saponified graft copolymer in 0.1, 0.5, 1.0, and 2.0% w/v of sodium chloride solutions was maximum at 120, 85, 60, and 47 g/g, respectively. An increase in cationic salt content in water reduces the water absorption due to a decrease in the osmotic pressure because the difference in the osmotic pressure between inside and outside the gel decreases.

9. Water absorption capacity of the saponified graft copolymer in 0.1, 0.5, 1.0, and 2.0% w/v of magnesium chloride solutions was maximum at 90, 44, 37, and 30 g/g, respectively. At the same concentration, magnesium chloride solutions have a lower absorption value than those of sodium chloride solutions. This suggests that the osmotic pressure equilibrium was reached earlier in the presence of the divalent ion.

10. Water absorption capacity 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 were maximum at 75, 90, 62, and 73 g/g, respectively.

11. Water absorption capacity of simulated urine was maximum at 76 g/g. Simulated urine solution is composed of the solutions of $CaCl_2$, $MgSO_4$, NaCl and urea. Divalent cationic salts in the simulated urine solution caused the HSPAN to decrease the water absorption capacity tremendously.

12. Water retention capacity in sand was 0.4 g/g. Mixtures of the sand with 0.5, 1.0, 2.0, and 3.0% of saponified starch-g-polyacrylonitrile could increase water retention gradually up to a maximum value of 431 g/g at 3.0% of the saponified polymer synthesized from 20 ml of acrylonitrile.

13. By including aluminium trichloride hexahydrate in saponified starch-g-polyacrylonitrile before precipitation by methanol, decreases in water absorption and wicking time were observed. Aluminium ions were absorbed by the carboxylate group on the surface of the HSPAN to form a chelating-like structure resulting in a linkage density at the surface particle greater than the linkage density in the interior particle. Because of the linkage density, the water absorption and wicking time was improved. The water absorption capacity was in the range of 550 to 160 times their original dried weight and the wicking time was in the range 15.30 to 0.30 minute depending on the aluminium salt content.

14. By using a freeze dryer for drying the HSPAN, the water absorption capacity increases considerably compared with that using a 65°C oven. The water absorption capacity of the freeze dried method was 682 g/g while that of the oven dried method was only 550 g/g times their original dried

weight. Heat drying induces the crosslinking between macromolecules that leads to the reduction of water absorbency.

As only the total dose can be controlled with the radiation source, it is found that at the fixed dose rate of 0.25 kGy/min, total dose 3.5 kGy and the 1:2 ratio of starch(g) and acrylonitrile(ml), the water absorption capacity of the so-produced saponified graft copolymer was 500 times their original dried weight. This graft copolymer was produced by using a sheet of aluminium foil for covering the inner wall of the irradiated vessel. The aluminium foil was probably regarded as the source of electrons that were emitted when gamma rays interacted with aluminium foil. These electrons contribute to an enhancing grafting reaction. Besides the role of aluminium foil, an acid condition such as nitric acid plays an important role in increasing grafting reaction and also the water absorption capacity. The irradiation in the acid medium leads to an increase in $G(H^{\bullet})$ that increases grafting sites on the starch backbone by the hydrogen abstraction reaction. The synergistic effect in increasing the water absorption capacity was further amplified by drying the saponified product with a freeze dryer. The water absorption capacity of the freeze dried method was increased to 682 times their original dried weight.

Suggestion and Future Work

There are many techniques to synthesize a high-water absorbing polymer by grafting vinyl monomers onto starch. The current synthesis technique is the simultaneous irradiation. The enhancement of grafting reaction brought in the increase in the the water absorption capacity. To develop high-water absorbing polymers to be used in agriculture and other applications, futher work should be carried out as follows:

1. Due to the instrumental limitation in configuration of the irradiation source of gamma rays, only total dose can be investigated at a fixed dose rate. Intensive research work elsewhere indicated that an optimum dose rate could enhance significantly a grafting reaction of this reaction. Modifications of the gamma source to make possible a certain variation in dose rate should be pursued to enhance the grafting reaction and high water absorption.

2. Study the mixed solvent of water on increasing grafting reaction such as methanol and ethanol. These solvents may render more efficiency in activating the trunk polymer by hydrogen abstraction processes.

3. Study the effect of comonomer such as vinyl acetate on grafting reaction and water absorption capacity. The G-value of vinyl acetate is 9.6-12 that is more than that of acrylonitrile ($G_{AN} = 5-5.6$) and the reactivity of vinyl acetate is 0.05 and that of acrylonitrile is 4.2. Thus, acrylonitrile may be grafted effectively on starch backbone.

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