

## CHAPTER V

### CONCLUSION and SUGGESTION

To carry out the research on the preparation of acrylic acid-cassava starch graft copolymer as a thickener for cotton fabrics printing under the reaction parameters, several attempts were used to pursue the possible techniques to acquire the suitable average molecular weights of the graft copolymers through the adjustment of water solubility of a conventional, highly water absorbing polymer, i.e. by decreasing the water absorption of hydrolyzed starch-g-poly(acrylic acid) to an extent of complete solubility. From all the experiments, the results can be concluded as the following:

1. Cassava starch-g-PAA copolymer was synthesized and confirmed by FT-IR spectroscopy. The absorption peak of the C=O stretching occurs at  $1,650\text{ cm}^{-1}$ , and the C=O and C-O asymmetry and symmetry stretching of carboxylate anions occur at  $1,575\text{ cm}^{-1}$  and  $1,415\text{ cm}^{-1}$ , respectively. The latter two peaks indicate that PAA grafts are converted into their organic salt(sodium polyacrylate) when the copolymer is saponified.

2. Cassava starch-g-PAA copolymer synthesized was also confirmed by the FT- $^{13}\text{C}$ -NMR spectroscopy. The chemical shifts at 172.15, 134.89, and 129.99, 62.74, and 35.83 ppm were assigned to the COOH, =CH<sub>2</sub>, =CH- of acrylic acid, respectively, and those of 64.72 and 35.83 ppm are for the -CH<sub>2</sub>- of a dimer of acrylic acid. The carboxylic acid groups in the copolymer are converted to carboxylate anions (COO<sup>-</sup>), appeared at 184.32 ppm, and the -CH<sub>2</sub>- group of a polyacrylate chain occurred at 45-46 and 50.27 ppm. The

chemical shifts at 99.21, 72.82, 76.94, 70.88, 71.15, and 60.21 ppm were assigned to the C<sub>1</sub>, C<sub>2</sub>, C<sub>3</sub>, C<sub>4</sub>, C<sub>5</sub> and C<sub>6</sub> of cassava starch, respectively. This confirms that acrylic acid has been grafted to the backbone of cassava starch.

3. By increasing the acrylic acid concentration, percentage homopolymer and the water absorption capacity of the saponified starch-g-PAA synthesized was in the range of 5 to 62 times their dry weights. The percentage graft copolymers were decreased from 95.9% to 87.6%

4. For the effect of hydrogen peroxide concentration on water absorption of the saponified starch-g-PAA copolymers in deionized distilled water, an increase in H<sub>2</sub>O<sub>2</sub> concentration higher than 1.94x10<sup>-2</sup>M, the water absorption was increased but percent graft copolymer was decreased, The values of percentage homopolymer at the H<sub>2</sub>O<sub>2</sub> concentration other than 1.94x10<sup>-2</sup>M were increased.

5. By using the starch content other than 60 g, increases the percent homopolymer formed, while the percent graft copolymer was decreased. The minimum water absorption of saponified starch-g-poly(acrylic acid) copolymers is 5 g/g while the maximum is 38 g/g. The percent graft copolymer was in the range of 91.5 to 95.9.

6. As a general rule of graft copolymerization, homopolymer formation usually accompanies grafting reaction at the expense of the graft copolymer. The percentage ascorbic acid at 0.33% is the optimum condition to create the minimum homopolymer formation. It produces the saponified starch-g-

poly(acrylic acid) copolymer with a water absorption of 5 times their original dry weight and the percent graft copolymer of 95.7.

7. With regards to the effect of reaction temperature on water absorption of the saponified starch-*g*-PAA copolymers, the reaction temperature increased from 25°C to 35°C, the water absorption decreased. An increase in the reaction temperature higher than 35°C, the water absorption was increased. When the temperature increased, a faster rate of H<sub>2</sub>O<sub>2</sub> decomposition was increased and it produces the oxygen gas, which is a radical scavenger due to its strong inhibition reaction. The chance of graft copolymerization of acrylic acid onto cassava starch is reduced. This results in the decrease of graft copolymer and homopolymer contents.

8. Regarding the effect of the reaction time on water absorption of the saponified starch-*g*-PAA copolymers in deionized distilled water, the reaction time increased from 2 h to 3 h, the water absorption decreased. An increase in the reaction time higher than 3 h, the water absorption was increased, the minimum water absorption is 5 g/g while the maximum water absorption is 41 g/g. The percentage graft copolymer was in the range of 93.5% to 96.3%.

9. Increasing the addition rate of monomer-initiator mixture increased the percentage homopolymer, as the adding rate increased, i.e. more radicals were generated in solution, which gave many short kinetic chain lengths of propagating chains. Then lower molecular weights of the grafted poly(acrylic acid) occurred. This was due to that homopolymer produced was higher than that of graft copolymer as the addition rate increases. The water absorption

capacity of saponified starch-g-poly(acrylic acid) was in the range of 5 to 29 times their original dried weight.

10. In this research, we utilized the glacial acetic acid and perchloric acid method to hydrolyze the graft copolymers in order to separate the acrylate side chains. But, there is a problem of separating the poly(acrylic acid) graft chains of the polysaccharide backbone, because no precipitate could be obtained. Thus, it is essential to determine the average molecular weights of poly(acrylic acid) grafted chains by GFC.

11. The average molecular weights of the fragments of the copolymers, grafted polyacrylate, obtained from the software of GPC program are in the range of 9,599-77,459 and 101,246-651,967 with the poly-dispersity from 1.01 to 3.47 (see Appendix B).

12. The rheological property of the thickener is known as shear thinning or pseudoplasticity, that is the viscosity decreases with increasing shear rates.

13. The relationship between the rheological properties of the water-soluble polymer and the salt concentration is governed by the charged characteristic of polymer chains. The viscosity of poly(sodium acrylate) was strongly influenced by the presence of sodium salt. It is evident that the presence of the salt significantly reduces the viscosity of poly(sodium acrylate). The amount of sodium salt in the grafted polymer chains increased with increasing the molecular weights of the grafted polyacrylate; the greater the salt content, the higher the water solubility and the lower the viscosity of the polymer solution.

### Suggestion and Future Work

There are many techniques to synthesize a thickener based on a grafting copolymerization of a vinyl monomer onto starch. In this work, a hydrogen peroxide-ascorbic acid initiation method is used. To develop further this type of thickener for textile printing applications, more investigations should be carried out as follows:

1. Instead of using acrylic acid as grafting monomer, methacrylic acid, vinyl acrylic acid and/or other unsaturated organic acids with an inherently stable structure and better thermal properties can also be tried.
2. Use other redox initiator systems such as, hydrogen peroxide/ferrous ion, potassium persulfate to develop a technique for another type of starch-based thickener.
3. The effect of oven dried and freeze dried methods on water absorption capacity of hydrolyzed starch-g-poly(acrylic acid) copolymer as a thickener can also be studied.
4. Other suitable methods to separate the polyacrylate graft chains from the polysaccharide backbone in order to determine the grafting parameters should be encouraged to study. These will give some insight information to regulate this type of material with lower water absorption.
5. The relationship between average molecular weights and viscosity, and qualities of printed cotton fabrics in terms of print quality and general

application should also be extensively investigated to justify the appropriateness of synthesis technique.

6. In this work, all the GFC chromatographs of the saponified starch-g-poly(acrylic acid) copolymers are similar. There are many peaks inseparable, due to the separation capability of the column materials and the length of the column, along with the type of the mobile phase. It is recommended that a slower flow rate of the mobile phase than the one presently used should be further investigated.

