

CHAPTER 5

CONCLUSION and SUGGESTION

5.1 Conclusion

The petroleum-based superabsorbent polymers are more attractive than the modified starch-based superabsorbent polymers due to their stability and longer service life. The major types of superabsorbent polymers, which apparently progressed beyond the laboratory and usually disclosed in the patent literature are poly(acrylic acid) salts, polyacrylamide, polyether-based nonionic xerogellants, hydrolyzed polyacrylonitrile, poly(vinyl alcohol-co-sodium acrylate), and poly(isobutylene-co-disodiummaleate). In this research, the copolymers of acrylamide(AM) and potassium acrylate(KA) were synthesized by inverse suspension polymerization and characterized the functional groups of the copolymer by FTIR. The spectrum reveals that the functional groups of the copolymer, which confirms the existence of the carboxylate and carboxamide functionalities, are similar to those of poly(acrylic acid) and polyacrylamide. These synthetic copolymers are used for improved handling of fine coal, water absorption in underground wet areas, agriculture, nappies, feminine hygiene products, incontinence pads, mineral processing, oil services, printing inks, coatings and specialties, paper and textiles, and pollution control. In 1993. The sales of the polyacrylates and polyacrylamides in Western Europe were 276 and 200 million dollars, respectively [80]. It is expected that the percentage revenue

increase of these polymers could reach 0.9 and 21.8% from 1993-2000 [81]. It is thus worthwhile to further pursue and develop this type of copolymer to achieve its higher efficiency in industrial applications. The present research can be concluded as follows:

1. The molar ratio of AM: KA, total monomer concentration and the cross-linking agent, N,N'-MBA were varied from 10: 90-90: 10 molar ratio, 5-7 molar and 0-0.075% mole N,N'-MBA, respectively, by using a thermal initiator $((\text{NH}_4)_2\text{S}_2\text{O}_8)$ of 1.4 g/l at 60°C in n-hexane as being organic phase. The total monomer concentration of 5 molar, the molar ratio of AM: KA at 60: 40, and the concentration of cross-linking agent at 0.025% mole provided a water-insoluble copolymer having the best water absorbency of 775 times its dry weight and a high water absorption time of 21.41 sec. However, cross-linking the superabsorbent with N,N'-MBA cannot improve water absorbency of the copolymer comparing to those without a cross-linking agent, but it conserved the gel strength of the copolymer beads probably due to an appropriate cross-link density in the copolymer.

2. The neutralization degree of acrylic acid from 40-100% were studied for polymerization of the total monomer concentration at 5 molar, 60:40 molar ratio of AM:KA with 1.4 g/l ($6.14 \times 10^{-3} \text{ M}$) $(\text{NH}_4)_2\text{S}_2\text{O}_8$, 1% w/v of suspending agent, Span 80 at various cross-linking agent concentrations. The appropriate neutralization degree of acrylic acid at 100% and 0.025% mole N,N'-MBA produced the best cross-linking copolymer having water absorbency of 775 g/g.

3. The concentrations of initiator $(\text{NH}_4)_2\text{S}_2\text{O}_8$ from 0.5-3.0 g/l (2.19×10^{-3} - $1.32 \times 10^{-2} M$) of the aqueous phase were carried out at the polymerization temperature of 60°C . It was found that polymerization initiated with the persulphate of 1.4 g/l ($6.14 \times 10^{-3} M$) provided the highest water absorbing copolymer possessing the water absorbency of 775 g/g.

4. The concentrations of the suspending agent (Span 80) from 0.5-2.0%w/v of the organic phase were performed at 60:40 molar ratio of AM:KA, total monomer concentration, 5 molar with the cross-linking agent concentration, 0.025% mole of monomer, 1.4 g/l ($6.14 \times 10^{-3} M$) $(\text{NH}_4)_2\text{S}_2\text{O}_8$, and 100% neutralized acrylic acid. It was found that the polymerization suspended with the suspending agent at 1.0%w/v gave the highest water-absorbing copolymer with the water absorbency of 775 g/g.

5. The cross-linked copolymers were also synthesized by inverse suspension polymerization with various types of suspending agent in the Span series. The water absorbency of the copolymer, synthesized with Span 80 was higher than the copolymers, synthesized with other Spans (Span 60 and Span 40), because the Span 80 has a high stabilization efficiency in n-hexane.

6. All of the synthesized copolymers were measured for the water absorbency by swelling in distilled water and saline solutions for water absorption and the water absorption rate. The best water-absorbing copolymer having water absorbency of 775 g/g in distilled water, was selected to test the effect of solution pH and salt concentrations upon water absorbency of the copolymer. The water absorbency of the copolymer was found to increase with increasing pH of

external solution until pH 5 and remained relatively unchanged afterwards because of the nature of copolymer as an anionic type of polymer and the osmotic pressure balance between inside and outside of the copolymer gel. In addition, the water absorbency of the copolymer decreases rapidly as the salt concentration increases due to the ionic strength of the solution, which affects the equilibrium osmotic pressure of the system. In case of the divalent, Mg^{2+} and Ca^{2+} ions, the osmotic pressure equilibrium should reach earlier than in aqueous potassium, and sodium solutions. The Mg^{2+} and Ca^{2+} ions may cross-link the gel by a salt formation with the carboxylate groups on adjacent chains or chain segments of the copolymer and lower the water absorbency comparing to that in aqueous potassium and sodium solutions.

7. The rheological properties of the copolymers were studied by viscosity measurement, from which shear modulus was calculated. The shear modulus of swollen gel increases with increasing cross-linking agent concentration. The swollen gel of the synthesized is a non-Newtonian substance (Pseudoplasticity) because the viscosity is dependent on the velocity gradient or shear rate.

8. The thermal properties of the copolymers were determined by DSC. The thermogram shows that the copolymer has two endothermic peaks. The T_{g1} is much lower than the reference T_g of polyacrylamide homopolymer at $165^{\circ}C$, whereas the T_{g2} is much higher than the reference T_g of poly(potassium acrylate), $194^{\circ}C$, possibly caused by the coating of the suspending agent on the surface of the copolymer beads. In addition, the type of suspending agent and the concentration of cross-linking agent affect the thermal properties of the copolymers, especially at the T_{g1} .

9. The surface morphology of the copolymer beads was studied by SEM. The SEM micrographs reveal that lumps are observed on the water-soluble copolymer beads, synthesized without the cross-linking agent, whereas the cross-linked copolymer beads are rather round in appearance. The cellular structure was found in the cross-linked copolymer that increased the surface areas of the copolymer which is useful for high water absorbency.

5.2 Suggestions for future work

Synthesis of superabsorbent polymers by inverse suspension polymerization would be further studied as follows:-

a) Other kinds of organic solvent should be used in the polymerization to synthesize the best superabsorbent polymer.

b) The influence of stirring intensity on the polymerization should be investigated.

c) Other kind of thermal initiators should be used in place of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ because when acrylic acid salt is polymerized with the water-soluble persulphate, cross-linking proceeds without using a cross-linking agent; in contrast, when the water-soluble azo-type polymerization initiator is used, cross-linking may occur with difficulties or unlikely to take place [82]. The examples of azo initiators include 2,2'-azobis-(N,N'-dimethyisobutyramidine) dihydrochloride, 2,2'-azobis-(2-amidino propane) dihydrochloride, 2,2'-azobis-

(N,N'-dimethyleisobutyramidine) dihydrochloride, 4,4'-azobis(4-cyanopentane carboxylic acid) and 2-carbamylazoisobutyronitrile.

d) Pore characteristics by Mercury porosimeter, and cross-link density of the copolymer beads are worthwhile to investigate for a complete understanding of its relationship to water absorption.

e) \bar{M}_c value, an influential parameter of the water absorbency should be made known for the extent of cross-link.

f) The molecular weight and molecular weight distribution of the primary chain should be carried out through pyrolysis or severe hydrolysis and its fragments were determined by traditional size-exclusion chromatography.

g) The mechanical properties of the superabsorbent polymer via uniaxial compression measurements could be determined for viscoelasticity evaluation such as Young's modulus, which is another parameter to indirectly correlate to cross-linking level.

h) The absorption capacity under pressure, stability, and safety test to be use for personal care application could be investigated.