

CHAPTER V

CONCLUSIONS AND SUGGESTION

5.1 Conclusion

5.1.1 Methyl methacrylate-divinylbenzene copolymer beads

The best toluene absorbent copolymer bead, the methyl methacrylate-co-divinylbenzene copolymer, was obtained by suspension copolymerization in the present research. The appropriate condition for synthesis to give the best toluene absorbent is

Monomer phase (0.14)

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|---|---------|
| - Methyl methacrylate-divinylbenzene ratio (94:6) | 95% wt |
| - Initiator concentration | 0.5% wt |
| - Crosslinking agent concentration | 0.1% wt |

Aqueous phase (0.86)

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|----------------------------------|---------|
| - Suspending agent concentration | 0.2% wt |
| - Reaction temperature | 70°C |
| - Reaction time | 5 hours |
| - Agitation rate | 140 rpm |
| - Toluene: Heptane (100: 0) | 100% wt |

All of chemicals used in this recipe are on the % weight based on the monomer phase. The resultant methyl methacrylate-divinylbenzene copolymer beads received from this recipe can be used to absorb toluene, which has the highest capacity of 15 times by volume.

The polymerization conditions influenced the morphology of the resultant bead copolymer are the monomer phase weight fraction, the concentration of suspending agent and the agitation rate. Very surprise, they did not influence the toluene absorption

fraction because at higher volume fractions, the concentration of continuous phase may be insufficient to fill the space between droplets and this is a reason for coagulation of droplets. The agitation and the nature of suspending agent influence the morphology significantly. In the first stage of suspension polymerization kinetic, the viscosity of the organic phase, the drop size, and the particle size distribution depend upon agitation and the nature of suspending agent. The water-soluble protective colloid or suspending agent decreases the interfacial tension between the monomer droplets and the aqueous phase to promote the dispersion and to reduce the droplet size. In order to prevent coagulation during suspension polymerization, especially during the second stage when particles become sticky, suspending agents or stabilizers are added to the reacting system. Suspending agent acts to require covering of the surface of the droplets, the amount of dispersing power depends upon the desired droplet size. In the suspension polymerization, monomer is suspended as liquid droplets in a continuous water phase by agitation. The polymerization conditions, especially stirring, influence the average particle size and distribution at this point and finally also the properties of the polymer suspension. An increase in the intensity of stirring usually leads to a decrease of the average size of the polymer particles due to the increase of the shear force at any droplet. When concentrations of the stabilizer used are such that the surface coverage is above the oil suspension, no tendency towards coalescence is exhibited when the stirring speed is much reduced.

The polymerization conditions influencing the swelling properties are the reaction time, the reaction temperature, the concentration of crosslinking agent, the concentration of initiator and the diluent composition. Generally, the swelling behavior is affected by three factors, which are rubber elasticity, affinity to the solution, and crosslinking density. In case of the higher thus amount of the crosslinking agent, the denser network of the copolymer is formed and reduces the \overline{M}_c , the average molecular weight between crosslinks. As mentioned earlier, the higher \overline{M}_c decreases the swelling ratio as was found in this study and elsewhere.

Increase in the initiator concentration in the free radical polymerization is to increase of the polymerization rate of the reaction. The crosslinking density was increased because the kinetic chain length was decreased. The kinetic chain length is

inversely dependent on the radical concentration or the polymerization. Also, the increasing initiator content caused the increasing crosslinking sites in the polymer network, the copolymer beads are then less flexible leading to the decrease in swelling ratio.

When the higher conversion or reaction time is higher, the polymer chains are more entangled and the second double bonds or vinyl groups of the crosslinking agent are then the crosslinking sites. When increasing the crosslinking sites, chain mobility inside the beads is restricted, it causes decreases in the swelling ratio.

The low temperature gives low conversion and low molecular weight of polymer. Divinylbenzene monomer has a higher reactivity than methyl methacrylate monomer, therefore it has many crosslinking sites in the copolymer, results in a higher crosslinking density and lower toluene absorbency. On the other hands, in case of high temperature, it usually give a high conversion and a lower molecular weight of polymer because of the increased polymerization temperature leading to the rate of the reaction, the rates of initiation, propagation, and termination. The further increase in the polymerization temperature reduces the molecular weight of the polymer due to an increase in the rate of termination and chain transfer, increase in the relative amount of the polymer chain end.

The resultant crosslinked methyl methacrylate-divinylbenzene copolymer beads do not dissolve in the toluene solvent but swell depending upon the degree of crosslinking density. Depending on the relative magnitude of the rate of polymer relaxation in response to the penetrating solvent to the rate of solvent diffusion, the swelling process may be Fickian or non-Fickian. Diffusion in polymer is complex and the diffusion rates should lie between liquids and solids. It depends strongly on the concentration and degree of swelling of polymer. The classification is according to the solvent diffusion rate and the polymer relaxation rate. In this work, the value n in all systems is close to 1, which indicates that the transport mechanism was case II or relaxation control. The diffusion of toluene solvent into poly[(methyl methacrylate)-co-divinylbenzene] spheres shows that the non-Fickian Case II type as the diffusion exponent, n , increased when the concentration of crosslinking agent divinylbenzene increased and the k_2 (the relaxation rate constant) slightly decreased when the concentration of divinylbenzene as a crosslinking agent was increased.

The diffusion coefficient of the toluene solvent into poly[(methyl methacrylate)-co-divinylbenzene] spheres was calculated by the short-time approximation as previously explained. The diffusion coefficient is almost constant in all systems is about 0.10-0.11 mm²/min and the concentration of crosslinking agent used in this work dose not effect the diffusion coefficient.

5.1.2 Butyl methacrylate-divinylbenzene copolymer beads

The effect of crosslinking agent and diluent composition on butyl methacrylate-divinylbenzene copolymer beads can be explained in the same way as those for methyl methacrylate-divinylbenzene copolymer beads. Most of the properties of butyl methacrylate-co-divinylbenzene copolymer give the same trend with methyl methacrylate-co-divinylbenzene.

5.1.3 Effect of third alkyl (meth)acrylate comonomer on the properties of methyl-methacrylate divinylbenzene copolymer bead.

Alkyl (meth)acrylates used in this study are butyl methacrylate, lauryl methacrylate, stearyl acrylate, and dodecyl acrylate. The nature of lauryl methacrylate, stearyl acrylate, and dodecyl acrylate are highly sticky which is not suitable for use as a porous bead by itself. The average particle size increased with increasing the hydrophobicity the material, but the average particle size of MMA-SA copolymer was smaller than the MMA-DA copolymer because the MMA-DA copolymer has the highest stickiness. The stickiness of MMA-DA was higher than MMA-LMA, MMA-SA, and MMA-BMA copolymer, respectively. The average particle size depends on the hydrophobic and stickiness properties.

The toluene absorbency was decreased when the polarity of copolymers was decreased; the toluene absorbency was found in the following order MMA-BMA > MMA-DA > MMA-LMA > MMA-SA. The highest capacity of MMA-BMA was 25 times of their original volume.

The capacity of oil absorption of methyl methacrylate-co-divinylbenzene copolymer bead is not affected by any reaction conditions. The effect of the third-

copolymer on oil absorbency of methyl methacrylate-divinylbenzene copolymer was found to increase when the hydrophobicity of third-comonomer increased.

5.2 Suggestions for future works

The oil absorption capacity of the synthetic copolymer of this study is not sufficient to use for oil absorbent due to their capacity is about 2 times of their original volume. It might be that the reaction conditions used in this study are not suitable for synthesis of the best oil absorbent. Even if the reaction conditions, such as the reaction time, the reaction temperature, the concentration of crosslinking agent, the concentration of suspending agent, the agitation rate, the monomer to aqueous phase, the concentration of initiator, and the diluent composition, had no influences on the oil capacity of beads copolymer (it was found in this study) but the appropriate concentration ratio between methyl methacrylate and alkyl (meth)acrylate was not studied in this present work. One thing of interest in the alkyl (meth)acrylate monomer is their hydrophobicity property that can improve the oil absorption capacity of terpolymer beads. In case of the higher concentration ratio of alkyl (meth)acrylate, the oil absorbency shall be improved. This should be a good research for further work to improve the oil capacity of methacrylate-divinylbenzene-alkyl (meth)acrylate terpolymer beads.

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