



CHAPTER III

DISCUSSIONS AND CONCLUSIONS

The polyamide microcapsules were synthesized via interfacial polycondensation by forming an oil-in-water emulsion in which the appropriate amounts of the diacid chloride and the emulsifier, under high shear from a homogenizer, produced a spontaneous emulsification and assisted in the longer stability of the microcapsules to be in form of emulsion. The emulsion so formed was utilized to produce the polyamide shell by combining with the aqueous diamine solution containing an acid-receiver. The steps of emulsification and formation of the microcapsules, the solutions/emulsions must be controlled at a specific temperature. Although sebacoyl chloride used in this work can dissolve very well in the encapsulated oil, dibutyl phthalate, it does decompose rapidly in the aqueous solution under the high kinetic rate and exothermically interfacial polycondensation. The use of sebacoyl chloride in the steps, therefore, must be controlled at 10°C. However, the solubility of terephthaloyl chloride was limited which led to the slower decomposition in aqueous solution and consequently resulting in a lower kinetic rate and an exothermical reaction to which the high temperature at 30°C was needed.

During the formation of microcapsule shells, it was essential that the temperature changes must be stringently controlled, otherwise, the shells would shrink and the encapsulated oil became expand. These behavior caused the poor formation of the thin film of the polymer shell on which the leakage was found in term of shorter life expectancy of the microcapsules.

From the literature reviewed and the experimental works done in

this thesis, the following conditions obtained from the preliminary tests were set for the entire work :-

1) Fixing the constant amount of chemical impurities, the mole ratio of the diacid chloride:the diamine:the acid-receiver was 1:1:2.

2) The oil-to-water ratio was 3:7 in the emulsification step and the emulsion-to-diamine solution ratio was 6:4 by weight.

3) The concentrations of the diacid chloride in the encapsulated oil for sebacoyl chloride was 1:29 to 5:25, whereas those for terephthaloyl chloride was 1:29 to 3:27 by weight. The amount of the diacid chloride was calculated from the extent of chemical impurities and the actual solubility of the diacid chloride in the encapsulated oil.

4) In the synthesis step, one must pour the emulsion, consisting of the encapsulated oil with the dissolved diacid chloride, into the diamine solution containing the acid-receiver under the control of temperatures for emulsification and interfacial polycondensation at 10°C and 30°C for sebacoyl chloride and terephthaloyl chloride, respectively.

5) The speeds of the homogenizer's propeller were at 2,000, 4,000, 6,000, 8,000, and 10,000 rpm. with the homogenizing time of 30, 60, 90, 120, and 150 sec. The emulsion after being highly sheared were poured immediately into the diamine solution in the presence of the acid-receiver to form the polymeric microcapsule shell.

6) After experimental section 2.8, each sequential experimental work was carried out based on the results from the previous experiments such as formulations of each phase, etc.

Experimental sections 2.3 - 2.7 were carried out to search for

the fundamental information so as to set the proper conditions for the syntheses of polyamide microcapsules as concluded above. From experimental section 2.8 onwards, the studies of influential factors affected the microcapsules synthesized and properties were summarized in the sequential order of the experiments as follows :-

1) Both sebacoyl chloride and hexamethylene diamine, and terephthaloyl chloride and para-phenylene diamine are the appropriate monomer pair for the syntheses of polymeric shell of the microcapsules with some inevitable different surface properties. The former pair gave a tough and flexible shell while the latter provided a hard and brittle crust. These difference was mainly due to the molecular structure of the polyamide shell in which the poly(hexamethylene sebacamide) shell consisted of an aliphatic backbone whereas the poly(para-phenylene terephthalamide) shell was composed of an aromatic skeleton.

2) Butyl acetate could not be used as good as dibutyl phthalate as encapsulated oil. Naturally, butyl acetate has a much higher vapor pressure and solubility in water than those of dibutyl phthalate; the properties of the former resulted in a failure in forming a continuous and smooth film for the microcapsules.

3) Poly(vinyl alcohol) was a powerful emulsifying agent in the syntheses of polyamide microcapsules, while sodium salt of styrene maleic anhydride copolymer could not be employed as an emulsifier since it could not form a stable emulsion of the encapsulated oil. Poly(oxyethylene lauryl ether) could not be used as well because of the coagulation formation during interfacial polycondensation. Sodium dodecyl benzene sulfonate was also excluded from the work as emulsifier due to lack of the formation of polyamide shell and incapable of encapsulating the oil.

4) Studies of the effects of propeller speed of the

homogenizer and homogenizing times on average particle size and particle size distribution, the microcapsules produced by the systems consisting of poly(hexamethylene sebacamide) and poly(para-phenylene terephthalamide) as polymeric shell, both using dibutyl phthalate as encapsulated oil and poly(vinyl alcohol) as emulsifier showed the same trends of results: Increasing the propeller speeds decreased the average particle size; and increasing the homogenizing times gave a more even size of the microcapsules which had not as yet been reduce in average size.

5) The reduction in the particle size with increasing the propeller speeds in the emulsification step affected the encapsulation efficiency of the encapsulant. For the case of poly(hexamethylene sebacamide) shell, the encapsulation efficiency was better than that of the poly(para-phenylene terephthalamide). The reasons for the latter was due to the hard and brittle shell which made part of the leakage of the encapsulated oil. In contrast, the poly(hexamethylene sebacamide) shell had a stronger, tougher and more durable surface to prevent the leakage of the encapsulant.

6) Increasing the emulsifier concentrations of poly(vinyl alcohol) in the syntheses resulted in the reduction of average particle size and brought about a more even particle size distribution. This can be explained in term of the lower surface tension of emulsifying droplets and stabilized the emulsified droplets. Besides, the effects also extended to the better encapsulation of the microcapsules as well as stabilized the whole system after the formation of the microcapsules, i.e., less coagulation.

7) The increase in the diacid chloride concentrations was to increase the shell thickness of the microcapsules which had a direct effect on the encapsulation efficiency without affecting the size of the

microcapsules. Reduction in the concentrations of the diacid chlorides in the case of poly(hexamethylene sebacamide) microcapsules produced the wrinkle and uneven microcapsules whereas more broken microcapsules were obtained in the case of poly(para-phenylene terephthalamide) microcapsules. The stoichiometric balances in materials were responsible for these observations.

8) The use of sodium dodecyl benzene sulfonate as an enhancing emulsifier for poly(vinyl alcohol) reduced drastically the average particle size of the polyamide microcapsules. Nonetheless, it increased the average particle size distribution. However, the increasing concentrations of this reagent reduce the encapsulating efficiency to a certain extent.

9) Any diacid chlorides and diamines could possibly be used to prepare polyamide microcapsules such as the monomer pairs of sebacoyl chloride and hexamethylene diamine; sebacoyl chloride and para-phenylene diamine; terephthaloyl chloride and para-phenylene diamine; terephthaloyl chloride and hexamethylene diamine; or even sebacoyl chloride, terephthaloyl chloride, hexamethylene diamine and para-phenylene diamine in an appropriate proportion. It was envisaged that these monomer pairs would produce quite significant different polymeric shells according to the differences in their molecular structures and chain flexibility.

10) In conclusion, the basic information obtained from several experimental works enables the improvement of stoichiometric balances and formulations for the syntheses of polyamide microcapsules. It is believed that this field is a combination of science and art. The compromise in various influencing factors helps improvement and govern the desired properties for a specific application of microcapsules.

The syntheses of microcapsules can be produced through the many existing techniques, nevertheless, the state-of-the-art technology of this area has been strongly emphasized the interfacial polycondensation, as this technique gives distinguished advantages over others as mentioned in the previous Chapters. This thesis is still on a fundamental basis for this only influential parameters are studied. It is hoped that this primary information may be the fundamental ideas for further developments in the microcapsule technology.

Based on the advantages of the interfacial polycondensation technique and emulsification system for synthesizing microcapsules, the following statements are for the further developments and applications of this field :-

1) Since the microcapsules can be synthesized within a short time in a batch dimension, therefore, a continuous production can be modified first in a laboratory scale.

2) For agricultural countries, pesticides and herbicides are necessary for developments of new crops and increasing productivity of agro-industry. Microencapsulation of such chemicals decreases their toxicity upon contact and controls the useful service life of the products through the release rate. The varieties of monomer pairs can be used for synthesis the different polymeric microcapsule shell, depending on the economical basis and efficiency of release rate.

3) The microcapsules for making carbonless copy paper can be synthesized by using the condensates which derive from petroleum and petrochemical processes as encapsulated materials.

The range of possible applications of microencapsulation is breathtaking. As with all new techniques, microencapsulation will find high its status and applications in the market place where it provides unique products; and thus specialty products should continue to expand.