



CHAPTER III

Results and discussion

Fragrance is a volatile chemical. It is used in various products such as laundry detergents, shampoo, deodorants, fabric softener, soap, body washes, cosmetic and etc. Many technologies have been developed to prolong the release of the fragrance materials. Encapsulation is a widely used technology because it is simple, cheap and adaptable in various applications. Encapsulation could reduce the degradation of fragrance and prolong its release. Furthermore, encapsulation can be done with minimal loss of fragrance, thus retaining the fragrance with maximal volume.

In this research, the fragrance encapsulation process was investigated. Citronellal was selected as a representative fragrance and ethyl cellulose was used as wall material. The compatibility of the obtained citronellal-encapsulated particles with various surfactants was investigated. In addition, the use of the fragrance encapsulated particles in various formulations of fabric softener was investigated. The stability and release profiles of the obtained softener products were also demonstrated.

3.1 Preparation of Essential oil-encapsulated nanoparticles

Citronellal encapsulated nanospheres were prepared by solvent coagulation, with ethyl cellulose as a wall material, under two different processes: stirring and ultrasonication.

3.1.1 Solvent coagulation method using stirring process

The obtained spheres appeared as cloudy aqueous suspension (Fig 3.1). The obtained suspension could be well dispersed in water. SEM and TEM photographs of the nanospheres obtained at the polymer concentration of 10,000 ppm showed spherical shape with a smooth surface (Fig 3.2 and 3.3 respectively). Particles obtained under stirring were microparticles with diameter about 1 micrometer (Fig 3.2). The obtained citronellal-encapsulated particles were formed by self-assembly of ethyl cellulose. It was speculated that when water was dropped into the polymer solution under continuous stirring, the hydrophobic parts of the polymer oriented themselves as interior of the particles, while the hydrophilic parts arranged themselves to the outer surface of particles, in order to have maximum interaction with water molecules, leading to the particle formation. The obtained particles (under stirring condition, at polymer concentration of 10,000 ppm) possessed diameter of 1455.7 ± 1.8 nm (Fig 3.4), with a polydispersity index (PDI) of 0.075 as determined by DLS (Table 3.1). The size of the dry particles was 900-1200 nm as determined by SEM.



Figure 3.1: The obtained suspension from self-assembly of polymer using stirring condition.

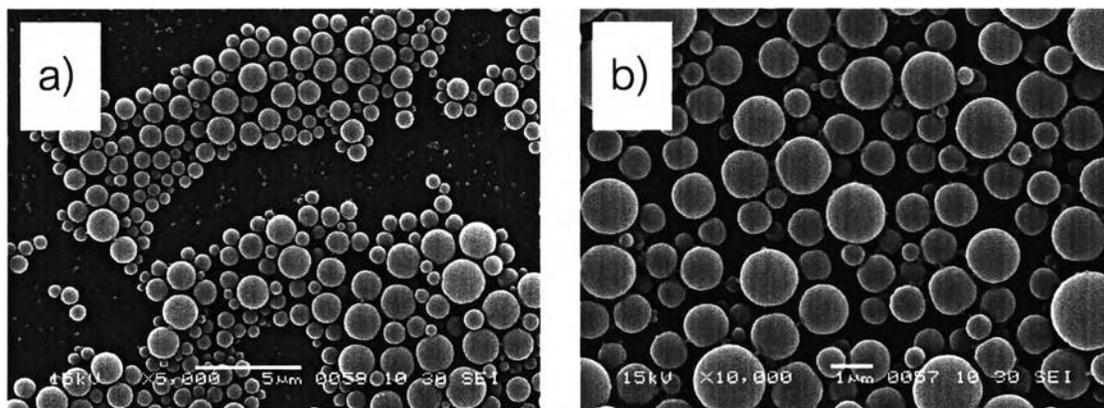


Figure 3.2: SEM micrographs at 15 kV of the suspension obtained under stirring condition, at polymer concentration of 10,000 ppm: a) at 5,000 x magnification, b) 10,000 x magnification.

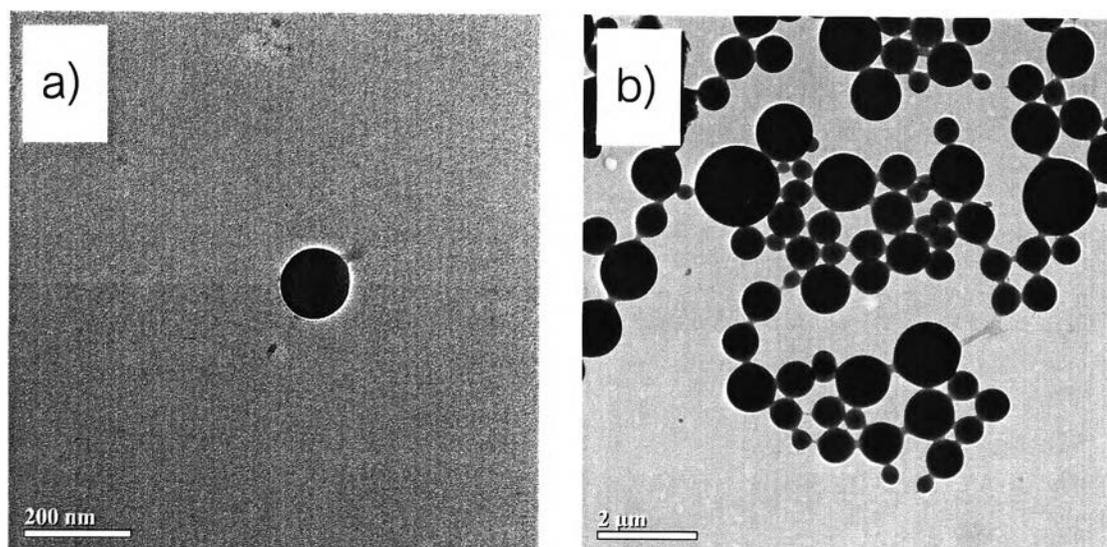


Figure 3.3: TEM photographs of the suspension obtained at polymer concentration of 10,000 ppm, with stirring: a) single particle, b) multi particles.

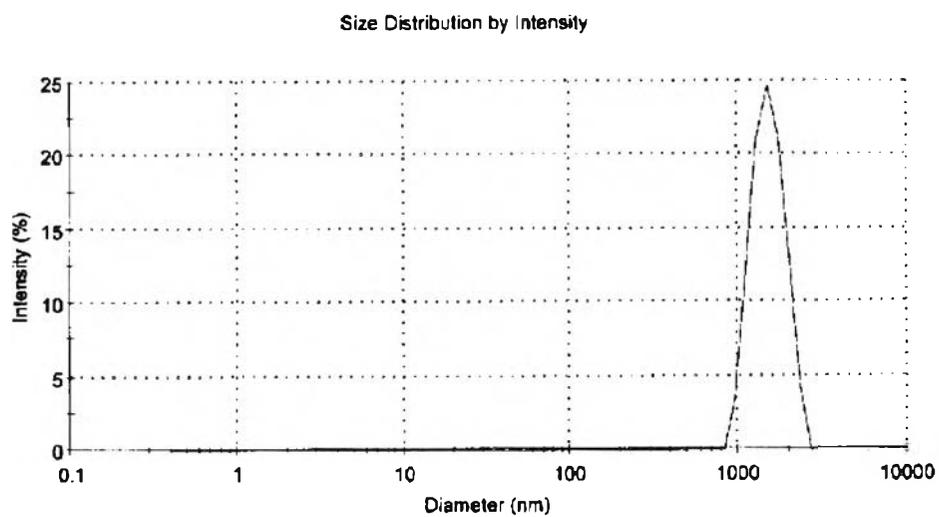


Figure 3.4: The particle size distribution of the suspension prepared under stirring condition, at polymer concentration of 10,000 ppm.

3.1.2 Solvent coagulation method using ultrasonic condition

The suspension obtained under ultrasonic process was milky white aqueous suspension (Fig 3.5). The particles could be held in solution for a long period of time with significantly less settling comparing to those prepared under stirring process. SEM and TEM photographs of the obtained nanospheres revealed spherical nanoparticles with better uniformity than those obtained from stirring method (Fig 3.6 and 3.7 respectively). Particles obtained with ultrasonic were nanosize with diameter of about 0.5 microns (Fig 3.6). The obtained fragrance-encapsulated particles possessed diameter of 580.3 ± 1.3 nm (Fig 3.8), with a polydispersity index (PDI) of 0.170 as determined by DLS (Table 3.1). The size of dry particles was 500-800 nm as determined by SEM.



Figure 3.5: The obtained suspension from self-assembly of polymer using ultrasonication process.

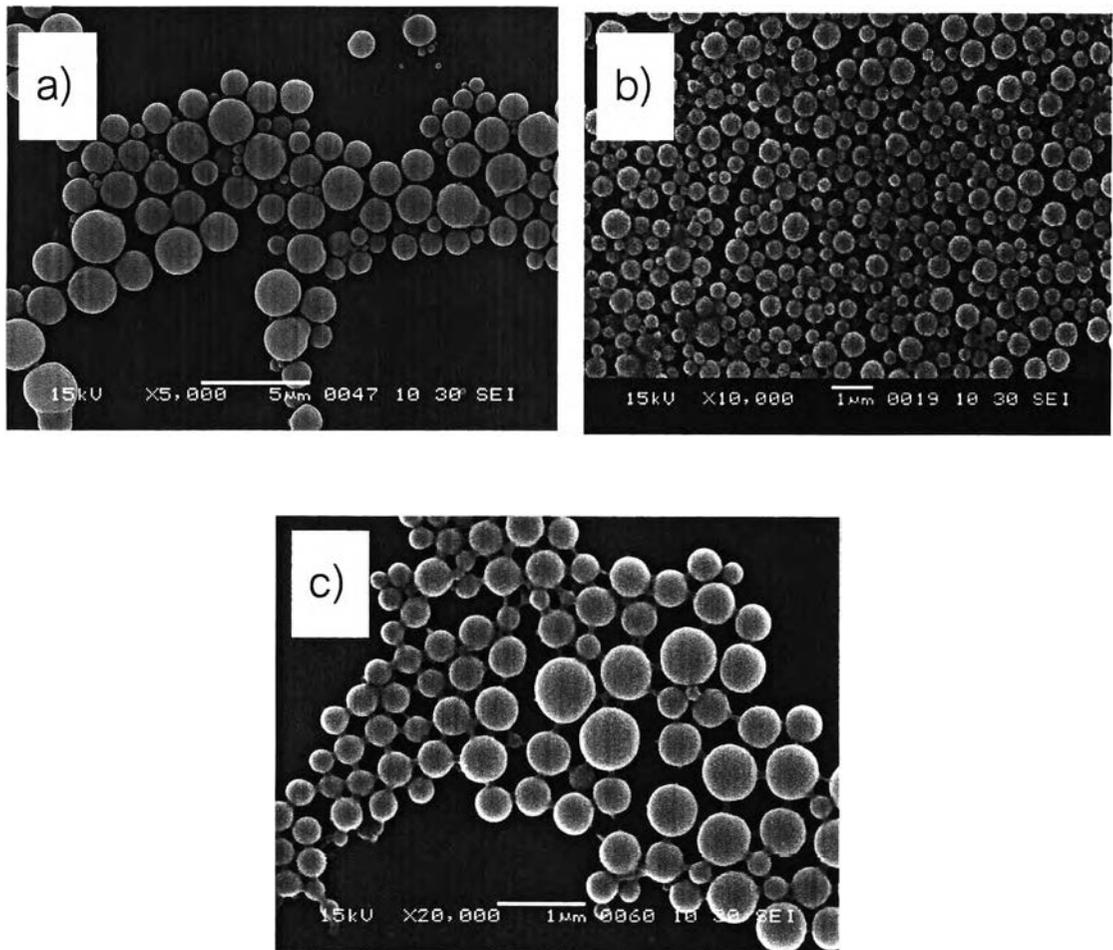


Figure 3.6: SEM micrographs at 15 kV of the suspension obtained from the ultrasonic process, at polymer concentration of 10,000 ppm: a) at 5,000 x magnification, b) 10,000 x magnification c) 20,000 x magnification.

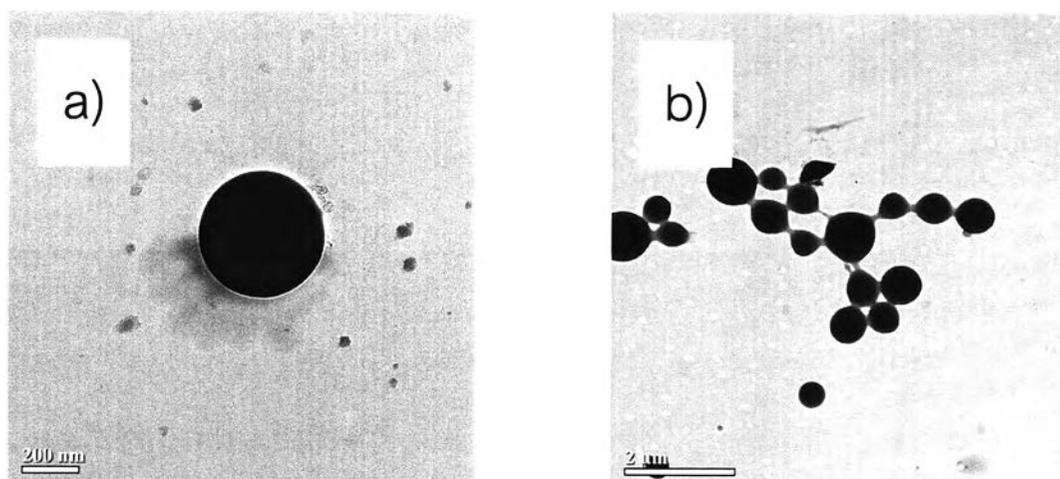


Figure 3.7: TEM photographs of the suspension obtained from the ultrasonic process, at polymer concentration of 10,000 ppm: a) single particle, b) multi particles.

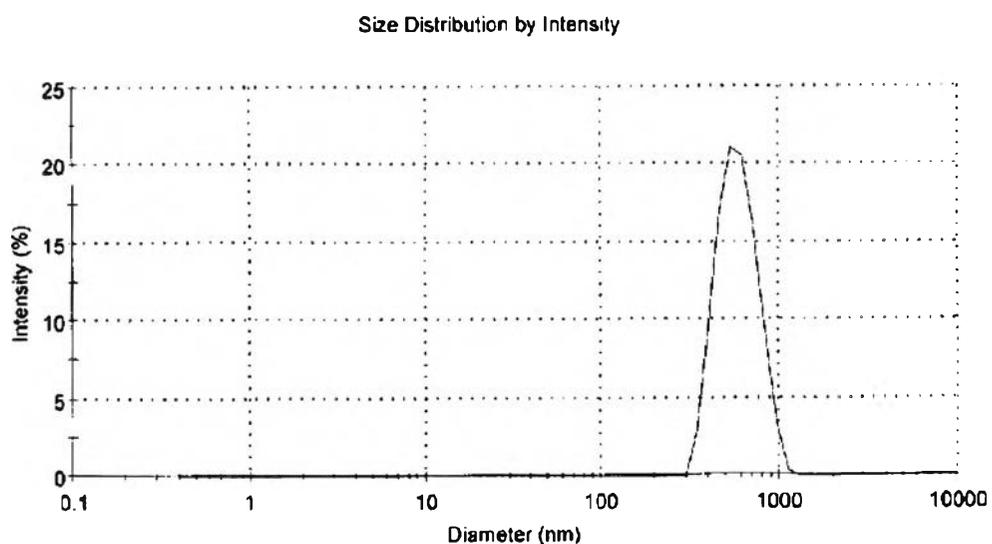


Figure 3.8: The particle size distribution of the suspension prepared under sonication condition, at polymer concentration of 10,000 ppm with ultrasonic condition.

Table 3.1 Sizes, shapes, and zeta potentials of the obtained suspensions prepared at polymer concentration of 10,000 ppm, using stirring process and sonication process.

| Condition of preparation | Shape | Average size by DLS | PDI | Size by SEM (nm) | Zeta potential (mV) |
|--------------------------|--------|---------------------|-------|------------------|---------------------|
| Stirring | sphere | 1455.7±1.8 | 0.075 | 900-1200 | -9.91±0.7 |
| Ultrasonic | | 580.3±1.3 | 0.170 | 300-800 | -8.76±1.3 |

The citronellal-encapsulated spheres obtained from the stirring process gave lower polydispersity index (PDI) than the colloid obtained with ultrasonic process. The result indicated that the suspension obtained from the stirring process was more homogeneous in size. The suspensions from the stirring process and from the ultrasonication process gave zeta potential of -9.91 ± 0.7 mV and -8.76 ± 1.3 mV, respectively (Table 3.1). A net charge of the obtained particle suspensions from both methods was negative.

However, as visually observable, the suspensions from stirring settled more quickly than those from sonication. Thus we have concluded that the sonication was a better process. This was the result of smaller particles. This settling property is very important for applications in various liquid products.

The rate of settlement of the particles was determined using turbidimeter. The freshly prepared suspension from the stirring process and from the ultrasonic process gave turbidity value of 6850 NTU and 8480 NTU, respectively. After 6 months the values were 3615 NTU and 6150 NTU for suspension from stirring process and sonication, respectively (Table 3.2). The

percentage of the difference clearly indicated that sonication gave suspension with better water dispersibility. The result agreed well with the visual observation discussed earlier.

Table 3.2 Turbidity value of the obtained citronellal-encapsulated suspension using stirring process and sonication at beginning and after 6 months

| Condition of preparation | Turbidity (NTU) | | % Different |
|--------------------------|-----------------|----------|-------------|
| | beginning | 6 months | |
| Ultrasonic | 8480 | 6150 | 27.5 |
| Stirring | 6850 | 3615 | 47.2 |

3.2 Compatibility of various surfactants to nanoparticles

After encapsulation of citronellal, dispersion of the obtained particles in aqueous surfactant was investigated. Seven types of surfactants including Arquad 2HT-75, Armosoft L, Texapon N 8000, Texapon N 70, EMAL AD-25, ECOLAT NP6 and Tween 80, were examined. They were selected as representatives of the three surfactants groups: cationic, anionic and nonionic surfactant. Arquad 2HT-75 and Armosoft L are cationic surfactant in the group of quaternary ammonium. Texapon N 8000 and Texapon N 70 are anionic surfactant in the group of sodium lauryl sulfate. EMAL AD-25 is anionic surfactant in the group of ammonium lauryl sulfate. ECOLAT NP6 is nonionic surfactant in the group of nonyl phenol. Tween 80 is nonionic surfactant in the

group of polyoxyethylene (20) sorbitan monooleate. The compatibility test was carried out at various surfactant concentrations (3, 5, 7 and 10 % w/v) using the citronellal-encapsulated spheres obtained from ultrasonication process, at the polymer concentration of 20,000 ppm. Physical appearances of the obtained mixtures were observed. The results are shown in Table 3.3.

All the obtained mixtures between citronellal-loaded particles and the seven surfactants (at 3, 5, 7, and 10 % w/v of surfactant) showed white homogeneous liquid at the beginning (Fig 3.9-3.15). Particles could be dispersed well in 5, 7, 10% w/v of Arquard 2HT-75 (Fig 3.9), 5, 7, 10% w/v of Armosoft L (Fig 3.10), 3 % w/v Texapon N 8000 (Fig 3.11), 3 % w/v Texapon N 70 (Fig 3.12), 3 % w/v EMAL AD-25 (Fig 3.13), 3, 5 % w/v ECOLAT NP6 (Fig 3.14) and 3 % w/v Tween 80 (Fig 3.15). At 3 % w/v of two cationic surfactants (Arquard 2HT-75 and Armosoft L), phase separation occurred in the third weeks. However, the problem could be solved by increasing surfactant percentage to 10 % w/v.

At 5, 7 and 10 % w/v of anionic surfactant (Texapon N 8000, Texapon N 70 and EMAL AD-25), precipitation of encapsulated particles could be observed in the first week.

At 7 and 10 % w/v of ECOLAT NP6, nonionic surfactant, phase separation occurred in the first week while at 3 and 5 % w/v, phase separation occurred after 3 weeks. Tween 80, another nonionic surfactant, precipitations occurred in the first week for the 7% w/v and 10% w/v surfactant samples. All samples showed precipitation at the 4th week.

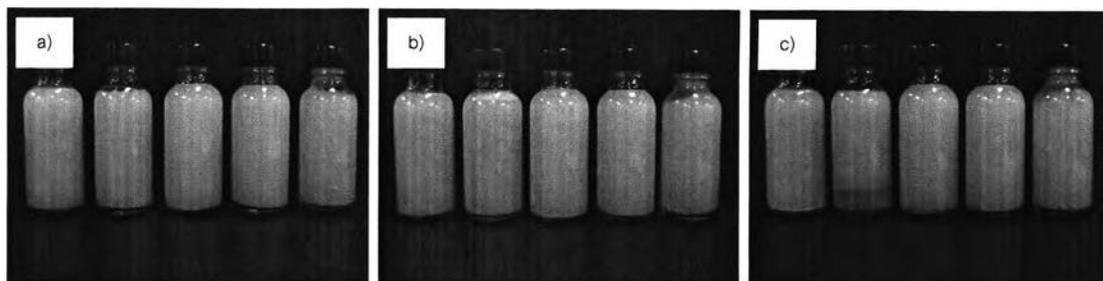


Figure 3.9: The mixture between nanoparticles and 0, 3, 5, 7 and 10 % w/v of Arquad 2HT-75 (left to right): a) initial time, b) first week and c) fifth week

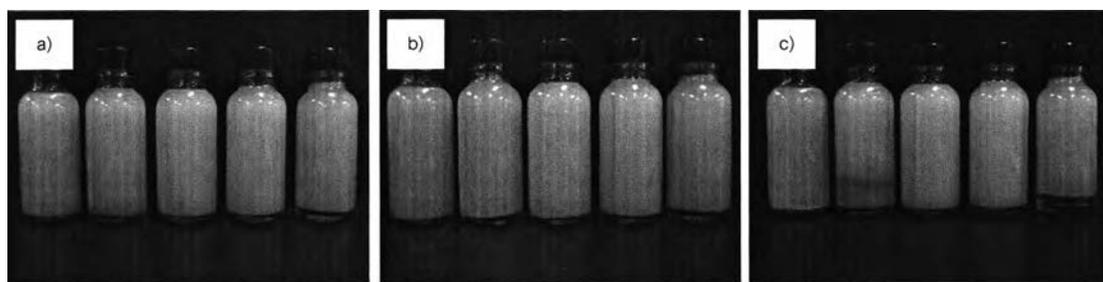


Figure 3.10: The mixture between nanoparticles and 0, 3, 5, 7 and 10 % w/v of Armosoft L (left to right): a) initial time, b) first week and c) fifth week

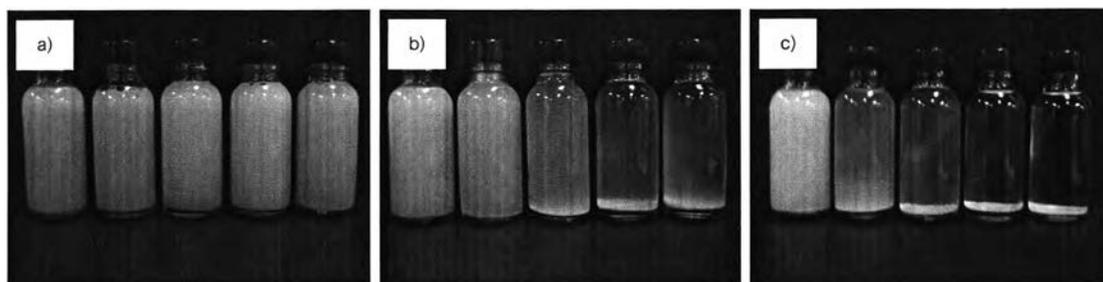


Figure 3.11: The mixture between nanoparticles and 0, 3, 5, 7 and 10 % w/v of Texapon N 8000 (left to right): a) initial time, b) first week and c) fifth week

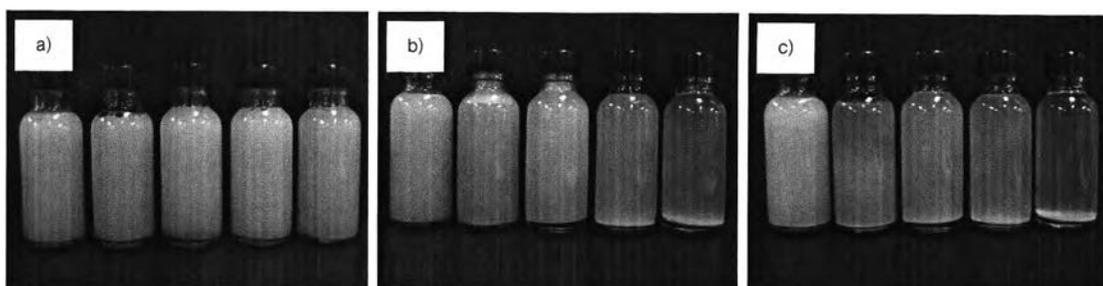


Figure 3.12: The mixture between nanoparticles and 0, 3, 5, 7 and 10 % w/v of Texapon N 70 (left to right): a) initial time, b) first week and c) fifth week

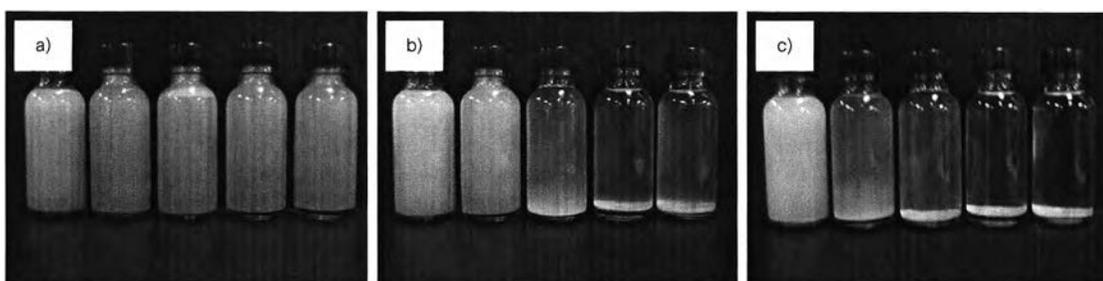


Figure 3.13: The mixture between nanoparticles and 0, 3, 5, 7 and 10 % w/v of EMAL AD-25 (left to right): a) initial time, b) first week and c) fifth week

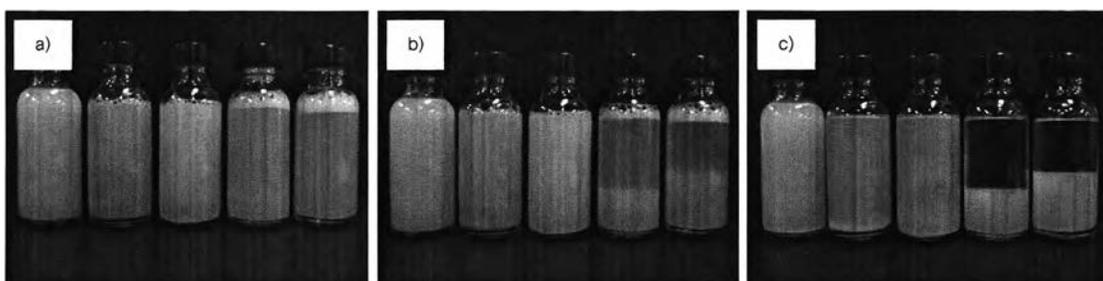


Figure 3.14: The mixture between nanoparticles and 0, 3, 5, 7 and 10 % w/v of ECOLAT NP 6 (left to right): a) initial time, b) first week and c) fifth week

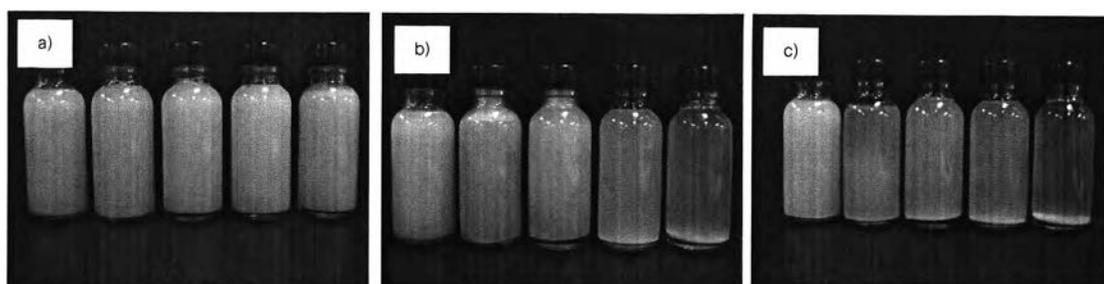


Figure 3.15: The mixture and nanoparticles and 0, 3, 5, 7 and 10 % w/v of Tween 80 (left to right): a) initial time, b) first week and c) fifth week

Thus it can be concluded that cationic surfactants are compatible with the citronellal-encapsulated spheres. As mentioned earlier that the zeta potential of the obtained suspensions was ~ -9 mV (Table 3.1) which indicated the negative surface charge. It is likely that the positive charge of the surfactant interacts well with the negative charge on the surface of the particles, thus help sustaining the dispersion. Layers of cationic surfactant around the spheres are probably responsible for the prevention of particle aggregation.

Table 3.3: Physical appearances of the mixtures between citronellal-encapsulated spheres and various surfactants.

| Type of surfactant | 0 week | | | | 1 week | | | | 2 week | | | | 3 week | | | | 4 week | | | | 5 week | | | |
|----------------------------|----------------------|---|---|----|----------------------|---|---|----|----------------------|---|---|----|----------------------|---|---|----|----------------------|---|---|----|----------------------|---|---|----|
| | Concentration (%w/v) | | | | Concentration (%w/v) | | | | Concentration (%w/v) | | | | Concentration (%w/v) | | | | Concentration (%w/v) | | | | Concentration (%w/v) | | | |
| | 3 | 5 | 7 | 10 | 3 | 5 | 7 | 10 | 3 | 5 | 7 | 10 | 3 | 5 | 7 | 10 | 3 | 5 | 7 | 10 | 3 | 5 | 7 | 10 |
| Cationic surfactant | | | | | | | | | | | | | | | | | | | | | | | | |
| 1. Arquard 2HT-75 | H | H | H | H | H | H | H | H | H | H | H | H | S | H | H | H | S | H | H | H | S | H | H | H |
| 2. Armosoft L | H | H | H | H | H | H | H | H | H | H | H | H | S | H | H | H | S | H | H | H | S | H | H | H |
| Anionic surfactant | | | | | | | | | | | | | | | | | | | | | | | | |
| 3. Texapon N 8000 | H | H | H | H | H | H | P | P | H | H | P | P | H | H | P | P | P | P | P | P | P | P | P | P |
| 4. Texapon N 70 | H | H | H | H | H | H | P | P | H | H | P | P | H | H | P | P | P | P | P | P | P | P | P | P |
| 5. EMAL AD-25 | H | H | H | H | H | P | P | P | H | P | P | P | P | P | P | P | P | P | P | P | P | P | P | P |
| Nonionic surfactant | | | | | | | | | | | | | | | | | | | | | | | | |
| 6. ECOLAT NP6 | H | H | H | H | H | H | S | S | H | H | S | S | H | S | S | S | H | S | S | S | S | S | S | S |
| 7. Tween 80 | H | H | H | H | H | H | P | P | H | H | P | P | H | P | P | P | P | P | P | P | P | P | P | P |

H = homogeneous liquid P = liquid with observable precipitates S = observable phase separation

3.3 Fabric softener formation

From compatibility tests, Arquad 2HT-75 and Armosoft L were best compatible with the citronellal-encapsulated nanospheres. As a result, fabric softeners were fabricated from these surfactants.

3.3.1 Preparation of fabric softener with free fragrance

The fabric softeners were formulated to contain 5 and 7 % w/v Arquad 2HT-75 and Armosoft L, respectively. Free-citronellal was added into the formulation at the final concentration of 30,000 ppm. The obtained formulation is viscous white liquid (Fig 3.16).

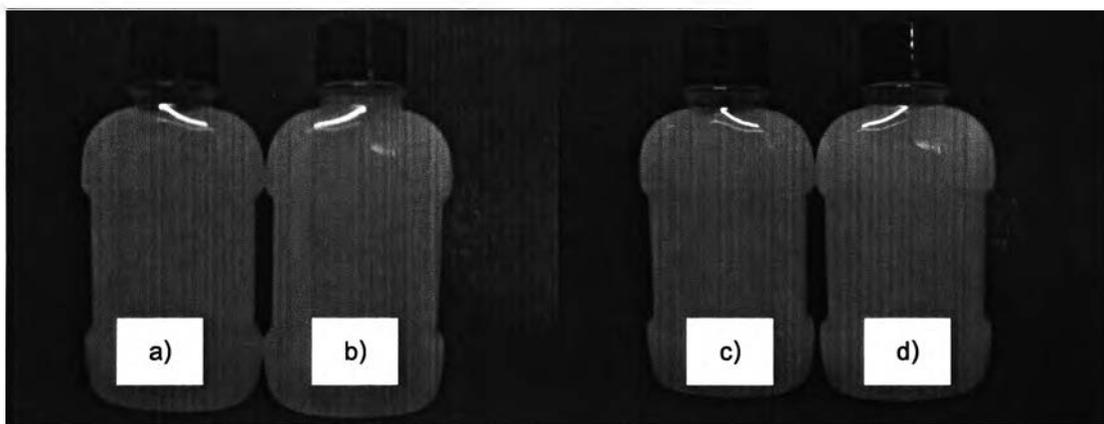


Figure 3.16: The various fabric softeners formulated with free citronellal using two surfactants at two percentages: a) 5% Arquad 2HT-75, b) 7% Arquad-2HT-75, c) 5% Armosoft L and d) 7% Armosoft L.

3.3.2 Preparation of fabric softener using encapsulated nanospheres

Similar fabric softener formulations were prepared but with citronellal-encapsulated spheres in place of free citronellal. The formulations were prepared to contain citronellal in the encapsulated state (10,000 ppm) and free citronellal (20,000 ppm). The obtained formulation showed viscous white liquid (Fig 3.17).



Figure 3.17: The various fabric softeners formulated with citronellal-encapsulated-spheres using various surfactants at various percentages: a) 5% Arquad 2HT-75, b) 7% Arquad-2HT-75, c) 5% Armosoft L and d) 7% Armosoft L.

3.3.3 Stability study of fabric softening

The purpose of a stability test is to ensure that a modified product meets expected physical and chemical properties when stored under appropriate conditions.

Accelerated stability study was designed to increase the rate of chemical degradation or physical change of active substance by using exaggerated storage conditions as part of the formal stability study. Data from these studies, in addition to long term stability study, can be used to assess longer term chemical effect at non-accelerated condition and to evaluate the effect of the short term excursion outside the storage conditions. A commonly accepted practice is to support the forecast obtained from accelerated stability testing by carry out periodic post-launch monitoring of retained samples stored at ambient temperature.

The stability of the obtained fabric softeners with free citronellal and with citronellal-encapsulated particles at four conditions, 25°C, 30°C, 40°C

and freeze/thaw, during a period of 1 year, were examined. The physical appearances of the fabric softeners were observed at appropriate times in order to predict their shelf-life.

At 25 °C and 30 °C, the visual observation indicated quite a homogeneous mixtures for all samples (Fig 3.18 and 3.19), even at the end of the test period (1 year). The particles dispersed well in both cationic surfactants, Arquad 2Ht-75, Armosoft L. We judged that the mixtures had shelf-life of at least 1 year.

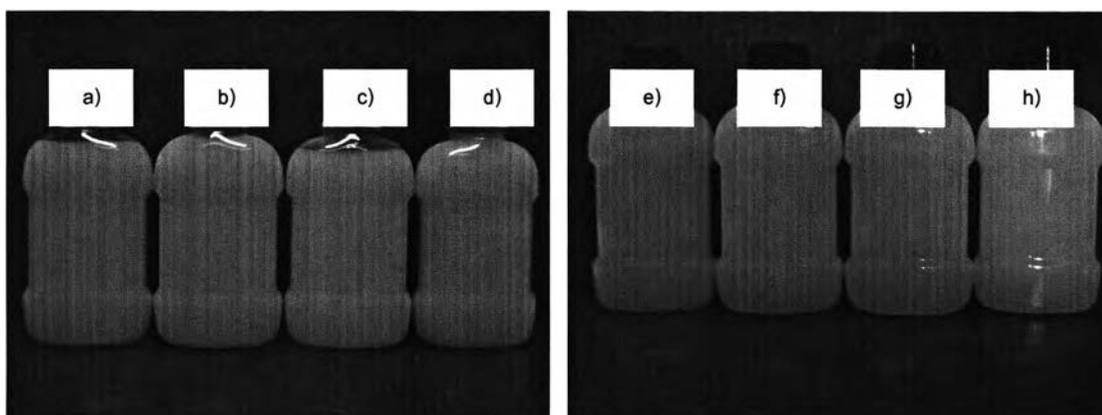


Figure 3.18: The pictures of fabric softeners prepared with different surfactants using free citronellal (left) and encapsulated citronellal (right) kept at 25 °C: a) 5% Arquad-2HT-75, b) 7% Arquad 2HT-75, c) 5% Armosoft L, d) 7% Armosoft L e) 5% Arquad-2HT-75, f) 7% Arquad 2HT-75, g) 5% Armosoft L and h) 7% Armosoft L.

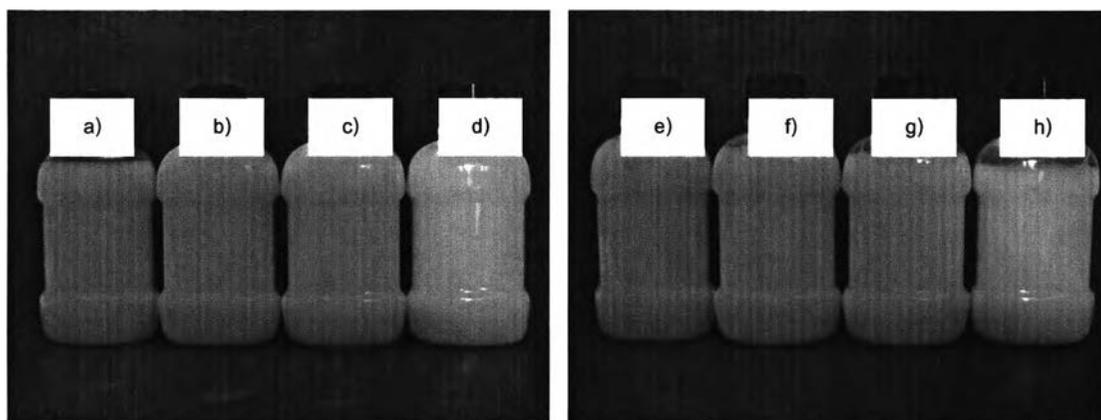


Figure 3.19: The pictures of fabric softeners prepared with different surfactants using free citronellal (left) and encapsulated citronellal (right) kept at 30 °C: a) 5% Arquad-2HT-75, b) 7% Arquad 2HT-75, c) 5% Armosoft L, d) 7% Armosoft L e) 5% Arquad-2HT-75, f) 7% Arquad 2HT-75, g) 5% Armosoft L and h) 7% Armosoft L.

At 40 °C which is an accelerated condition, after 1 year, the visual observation indicated quite a homogeneous mixtures for all samples (Fig 3.18 and 3.19), even at the end of the test period (1 year). The particles dispersed well in both cationic surfactants, Arquad 2Ht-75, Armosoft L. We judged that the mixtures had shelf-life of at least 1 year.

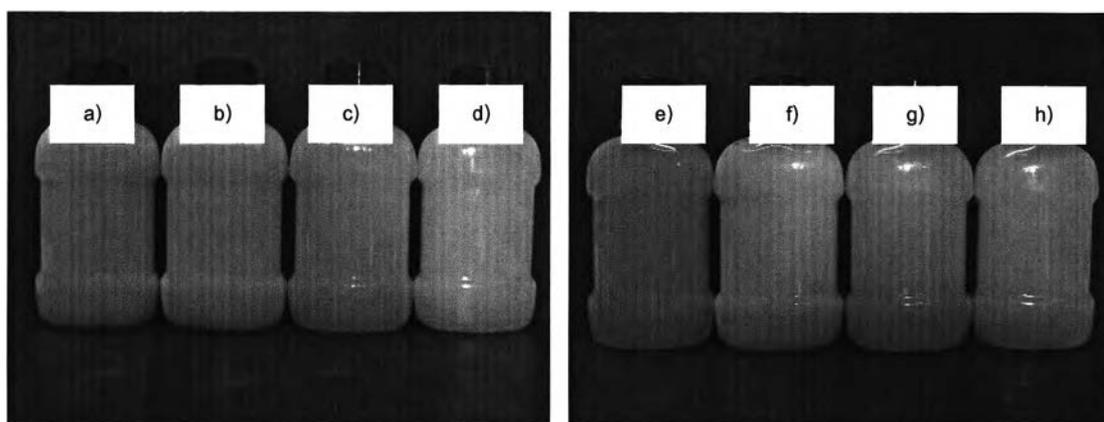


Figure 3.20: The pictures of fabric softeners prepared with different surfactants using free citronellal (left) and encapsulated citronellal (right) kept at 40 °C : a) 5% Arquad-2HT-75, b) 7% Arquad 2HT-75, c) 5% Armosoft L, d) 7% Armosoft L e) 5% Arquad-2HT-75, f) 7% Arquad 2HT-75, g) 5% Armosoft L and h) 7% Armosoft L.

Since the product may encounter extreme temperature during storage and transport, the freeze/thaw stability test was studied. All the 3-cycle-frozen/thawed-samples showed homogeneous appearance excepted that the FARM5 sample (5% w/v Armosoft L) showed phase separation (Fig 3.21). Since the phase separation was observed in only sample prepared with free citronellal, while the similar formulation prepared with encapsulated citronellal showed no phase separation, it was concluded that the encapsulated particles could increase the stability of fabric softener formulation.

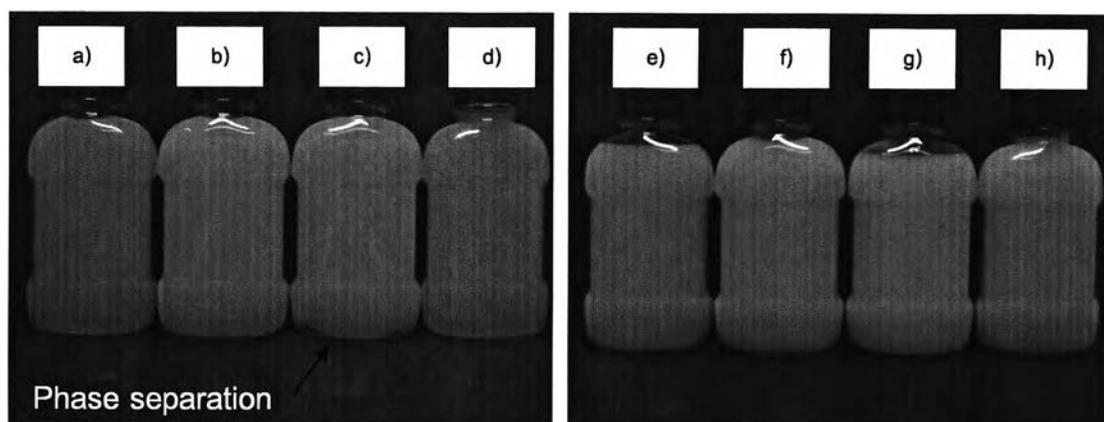


Figure 3.21: The pictures of fabric softeners prepared with different surfactants using free citronellal (left) and encapsulated citronellal (right) kept under freeze/thaw: a) 5% Arquad-2HT-75, b) 7% Arquad 2HT-75, c) 5% Armosoft L, d) 7% Armosoft L e) 5% Arquad-2HT-75, f) 7% Arquad 2HT-75, g) 5% Armosoft L and h) 7% Armosoft L.

3.4 Release profiles

Four fabric softeners with citronellal-encapsulated spheres and four of those with free citronellal were applied onto the cotton fabrics and the treated fabrics were subjected to 30 day-release study, using headspace gas chromatography/mass spectroscopy. The release profiles clearly indicated better fragrance prolongation in the formulations using citronellal-encapsulated spheres. In addition, different types of surfactants whether Arquad 2HT-75 or Armosoft L, slightly affected the sustainability of citronellal. The fabric treated with softener formulated with Arquad 2HT showed better fragrance prolongation than that formulated with Armosoft L (Fig 3.22 and Fig 3.23). This may be a result of better interaction between Arquad 2HT-75 and citronellal molecule, since its effect could also be observed in both the formulations with free citronellal and the formulations with encapsulated citronellal.

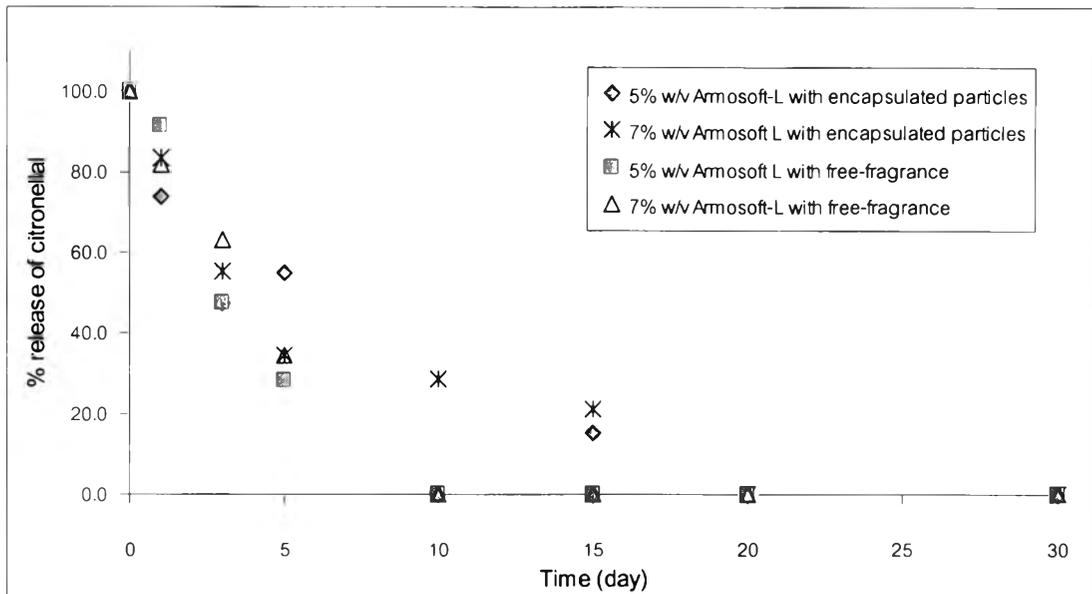


Figure 3.22: Release profiles of fabric softeners formulated with Amosoft L.

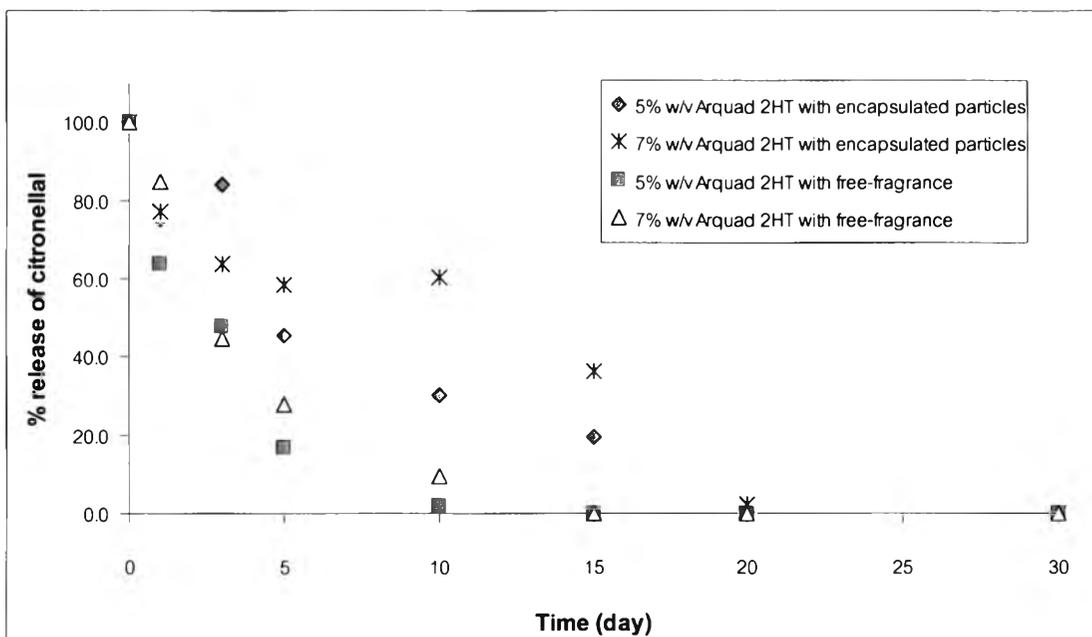


Figure 3.23: Release profiles of fabric softeners formulated with Arquad 2HT-75.