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# Polymer dispersion preparation by flow induced phase inversion emulsification

## Part 1 *The effect of silica on emulsification and dispersion characteristics*

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Low density polyethylene (LDPE) melt was emulsified in the presence of a hydrophobically modified water soluble polymer (HMWSP) and colloidal hydrophilic silica using the Flow Induced Phase Inversion (FIPI) emulsification technique. HMWSP was used as the surface active material. After the emulsification, LDPE melt was solidified to obtain a polymeric dispersion. Silica was used to aid the emulsification and improve the emulsion/dispersion characteristics. It was shown that the presence of silica increases the amount of aqueous phase necessary for phase inversion from water-in-LDPE melt to LDPE melt-in-water emulsion. The mean particle size and particle size span increased in the presence of silica. However, due to broader particle size distribution, the viscosity was lowered. The dispersions with silica appeared to form a more uniform film compared with the dispersion without silica. When the silica concentration is less than 1% in aqueous phase, an emulsion is obtained. At 2% silica level, a wet powdery material is obtained. This material can be diluted to obtain a dispersion or it could be used in powder coating. © *2000 Kluwer Academic Publishers*

## 1. Introduction

In our previous study on the phase inversion emulsification of thermoplastics, we have shown that colloidal low density polyethylene or ethylene vinyl acetate latexes could be obtained using hydrophobically modified water soluble polymers (HMWSPs) as surface active agents [1]. It has been shown that the molecular architecture of the HMWSPs is also important in the emulsification efficiency (particle size of the emulsion and emulsion yield and amount of HMWSP used to achieve a given yield). After phase inversion emulsification, because of the very low level of water content (∼20%), the resulting emulsion needs to be diluted before the polymer melt droplets can be solidified using low rates of deformation during cooling. Nevertheless, the emulsions even at 40% water content are relatively viscous and tend to form a skin upon standing. It is also important to note that the molecular surfactants could not be used to emulsify polymeric melts [1].

The mechanisms of flow induced phase inversion (FIPI) emulsification applied to melt [1] and polymeric resins [2, 3] indicate that in order to obtain small, monodispersed droplets/particles, the phase inversion should be carried out at high dispersed water phase volumes and the aqueous phase viscosity should be high. The technique described in references [2, 3] makes use of the water entrapped within surfactant lamellar bilayers during the dispersion of water in polymeric resins. During this stage, multi-lamellar vesicles are formed in the aqueous phase. Due to water entrapment between the bilayers, the aqueous phase viscosity increases, thus the dispersion of the aqueous phase in the polymeric resin is facilitated, leading to smaller aqueous phase droplets (i.e. larger interfacial area which is maintained after phase inversion). Furthermore, during phase inversion, large stresses can be developed leading to smaller droplets with a narrow size distribution.

After FIPI emulsification [2–5], multi-lamellar surfactant vesicles appear to deposit on the polymeric resin droplets which result in a drop in the emulsion viscosity and conductivity. Nevertheless, these emulsions are highly stable (i.e. unseparated after 3 years), presumably due to the highly effective stabilisation by the surfactant deposited on the surface of the emulsion droplets. In essence, the above emulsification procedure utilizes the interaction between the surfactant and water to advantage during the various stages of emulsification and subsequent emulsion life.

Because molecular surfactants cannot be used in the emulsification of thermoplastics [1], the above technique cannot be utilized. In the case of thermoplastics, macromolecular surfactants (which are successfully used as emulsifiers) do not form well ordered lyotropic liquid crystal structures capable of large amounts of water entrapment and subsequent deposition on the polymer melt droplets or latexes after solidification. Furthermore, high deformation rate flow will tend to form a collapsed state of the macromolecular surfactant. Therefore, these advantages presented by molecular surfactants are not apparent in macromolecular surfactants.

This disadvantage can be overcome if we now consider the interactions between macromolecules and colloidal particles such as colloidal silica, as well as the interaction between silica and water. Due to the presence of surface hydroxyl groups in hydrophilic silica and its large surface area, water is attached to silica and a 3D gel network is formed, thus increasing the viscosity of the dispersion even at very low silica loadings [6–8]. Silica can also be used as a reinforcing agent in certain polymers, in order to enhance their mechanical, electrical and surface finish characteristics [6–12]. However, mixing of hydrophilic silica with thermoplastics such as polyethylene and polypropylene requires considerable mechanical work. Consequently, polymer molecules undergo chain scission and subsequently form irreversible bonding with the filler (silica). As a result, the reacted polymer cannot be removed from the filler surface and it is known as "bound polymer" [6, 7, 13–15]. More polymers can deposit on the filler surface in which the driving force for the deposition is entropic in nature as a result of flow induced molecular orientation and extension [6, 7, 13, 14]. The thickness of the bound polymer is typically a few nanometers [6, 7] although it depends heavily on the molecular weight of the polymer, the molecular architecture (degree of branching, linearity) and the flow conditions. During the course of these processes, the initially hydrophilic silica becomes hydrophobic due to the formation of bound polymer. The chemical and X-ray examinations of bound polymer indicate the formation of carbonyl groups in the polymer and due to the conformational restrictions on the polymer chains, substantially lowered crystallinity compared with the bulk polymer is observed [6, 7, 14, 15].

Because of the ability to adsorb macromolecules rapidly, silica (or any other high specific surface area particles) was used as "crumbling agents" (i.e. materials to phase invert (particle-in-polymer melt) dispersions to [(particle-in-polymer melt)-in-particle] state to form agglomerates) in the intensive agglomeration/microencapsulation of powders using high molecular weight polymers in the molten state [6, 7, 14–16].

It is also well known that small particles can be used to stabilise dispersions, the best known example being provided by food emulsions such as butter, margarine and low-fat spreads in which fat crystals stabilise the aqueous phase/oil phase interface. Silica particles have also been used to stabilise the oil/water interface in emulsions [13, 17, 18]. The stabilisation mechanism in this type of emulsion is the formation of a mechanically strong interfacial core which prevents film drainage as two droplets approach each other with the potential to coalesce. Therefore, the presence of silica at the interface of the polymer melt can be useful to stop droplets coalescing during cooling (often carried out while mixing) thus preventing phase re-inversion from polymer melt-in-water to water-in-polymer.

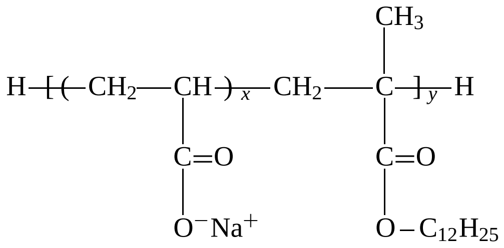
The above argument indicates that the silica/polymer melt and silica/water interactions can be utilised in the same way as the surfactant multi-lamellar vesicles are utilised to achieve a more efficient emulsification process, more stable emulsion and probably a superior product.

## 2. Experiment

### 2.1. Materials

i. Low density polyethylene (LDPE) supplied by EXXON, coded ESCORENE MFI155, with $M_n = 40000$ and density 920 kg/m$^3$.

ii. Surface active agent A-2 is an experimental Hydrophobically Modified Water Soluble Polymer based on poly(acrylic acid) sodium salt and supplied by National Starch & Chemical Company. This was in the form of 25% solid by weight in water and solution pH was 4.2. It is partially (80%) neutralised with sodium hydroxide. These materials are also used in the stabilisation of dispersions as viscosity modifiers etc. [1, 19]. The chemical structure of A-2 is shown below:



$$\mathrm{H}-\left[\left(\mathrm{CH_2}-\underset{\substack{|\\ \mathrm{C=O}\\ |\\ \mathrm{O^-Na^+}}}{\mathrm{CH}}\right)_x-\mathrm{CH_2}-\overset{\substack{\mathrm{CH_3}\\ |}}{\underset{\substack{|\\ \mathrm{C=O}\\ |\\ \mathrm{O-C_{12}H_{25}}}}{\mathrm{C}}}\right]_y-\mathrm{H}$$

where $x = 8$, $y = 3$.

iii. The fumed hydrophilic silica powder Aerosil 380 was supplied by Degussa. The average primary particle diameter is 7 nm and the surface area is 380 m$^2$/g. In the preparation of silica gel, a known amount of Aerosil 380 powder was mixed with distilled water. The concentration of silica in water was fixed at 1.0, 2.0 and 5 wt%.

### 2.2. Equipment

#### *2.2.1. HAAKE high torque mixer: Rheocord 9000*

Emulsions were prepared using a high torque mixer (HAAKE Rheocord 9000). It consists of a horizontally mounted, heavy duty motor drive together with a torque sensor which is attached to mixing heads, two roller type rotors. These two rotors rotate at 2 : 1 speed ratio within adjoining cylindrical cavities, and they produce a relatively high shear rate, and a complex deformation pattern which involves alternate shearing/elongation and relaxation. The material flow inside this mixer is not uniform. Therefore, the details of the flow pattern will depend on the rheological properties of the fluid under study and depend mainly on the viscosity of the continuous medium, and the dispersed phase: particle size, shape and concentration. During the experiment, the temperature of the mixer can be controlled using an air cooling system. The torque on the rotors, temperature and the speed of the rotor are recorded as functions of time, therefore, the full emulsification history can be profiled. In the experiments reported here a constant rotor speed (60 rpm) was used. The torque data reported here was expected to give an insight into the phase inversion emulsification process as shown previously [1, 6, 7, 14–16].

### 2.2.2. *Scanning electron microscopy (SEM)*

Morphology studies of films formed by the emulsions were carried out using a Hitachi S-2400 Scanning Electron Microscope. Emulsion samples were prepared for SEM by drying a drop of emulsion on a specimen mount. Agglomerated powder samples were fractured in liquid nitrogen then stuck onto stubs using double sided conductive adhesive tape. The emulsion film sample was prepared by putting one droplet of emulsion on a flat glass slide and then spreading it evenly on the glass surface. The sample was dried overnight. Afterwards the sample was placed into an oven and heated up from room temperature to 135°C over a period of 20 minutes and then kept at this temperature for half an hour. Afterwards, the sample was allowed to cool down to room temperature within the oven over a period of 4 hours.

All the samples were carbon-coated prior to observation.

### 2.2.3. *Environmental SEM*

A Philips XL30ESM-FEG Environmental SEM was used to examine the wet emulsion and observe particle aggregation as water evaporated. This technique can therefore give the dynamics of film formation from wet emulsions.

### 2.2.4. *Diffractometer (X-ray)*

Emulsion film samples were prepared as in (2.2.2). The crystallinity of the films were measured from the diffractometer traces made using a Philips X-ray generator PW1050, operated at 50 kV, 25 mA and using Cu radiation.

The crystallinity of the LDPE emulsion film can be determined by measuring the fraction of crystalline region in the sample [20].

### 2.2.5. *Particle size and size distribution analysis*

The particle size and size distribution analyses were performed using a Malven Mastersizer in which the laser diffraction technique is employed. From the measurement of particle size distribution, various mean particle sizes (such as the volume average $D\,[4,3]$, and surface average $D\,[3,2]$ mean particle sizes) are computed. The width (spread) of the size distribution is characterised by particle size span defined as

$$\text{Span} = \frac{D[v,0.9] - D[v,0.1]}{D[v,0.5]}$$

where $D[v,0.9]$, $D[v,0.5]$ and $D[v,0.1]$ are the diameters below which 90, 50 and 10% of the particles lie respectively. The particle size distribution as well as various particle sizes are computed by using the software available in the Malvern Mastersizer.

### 2.2.6. *Viscosity measurement*

The variation of viscosity with shear rate was measured using a HAAKE Viscotester VT 550 with the coaxial cylinder system. Temperature was kept at 25°C.

## 2.3. Emulsion preparation

A typical method of emulsion preparation is as follows. 100 g LDPE granules and 100 g of A-2 solution (containing 25 wt% HMWSP) were mixed together in a beaker. The mixer was set to heat up to 120°C and when the temperature had reached 60°C the rotor was turned on (60 rpm) and the mixture added in. The torque value was very low at the beginning because of the high water content. As temperature continued to increase the torque increased as a result of the loss of water by evaporation while the polymer melted. The torque rose rapidly and finally reached a maximum value. At this point, a glass reflux condenser cooled with tap water was fixed on the mixer. Then pure water or silica gel at room temperature was titrated into the mixer. The addition of water resulted in a steady drop in the mixer torque, indicating the presence of some free/unincorporated water. The rate of dosing of aqueous phase was approximately 1.5 g per minute. During water or silica gel addition, the temperature fell as well but at a low addition rate it was kept at 102°C, well above the LDPE crystal melting temperature of 86°C. When the water concentration reached a certain value, LDPE melt-in-water emulsion was formed. The emulsification histories of LDPE melt-in-water are shown in Figs 1–4. The aqueous phase fraction at phase inversion is denoted by $\phi^*$ (defined as weight of aqueous phase/total weight).

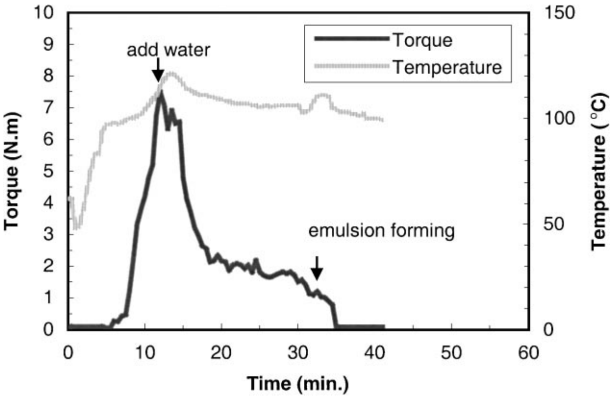


*Figure 1* Variation of the mixer torque and emulsion temperature with time during the phase inversion emulsification of LDPE in the absence of silica. Aqueous phase fraction at phase inversion was $\phi^* = 0.20$.

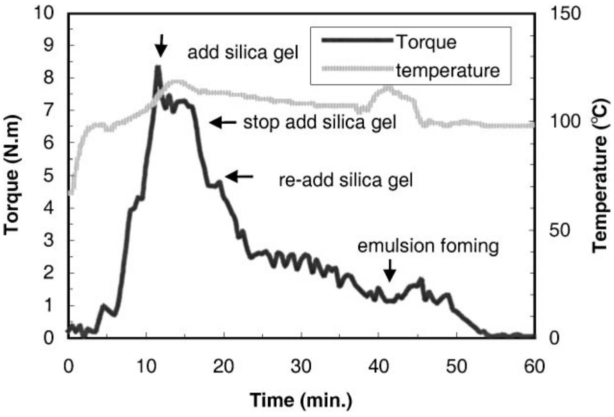


*Figure 2* Variation of the mixer torque and emulsion temperature with time during the phase inversion emulsification of LDPE in the presence of 1% silica in aqueous phase. Aqueous phase fraction at phase inversion was $\phi^* = 0.27$.

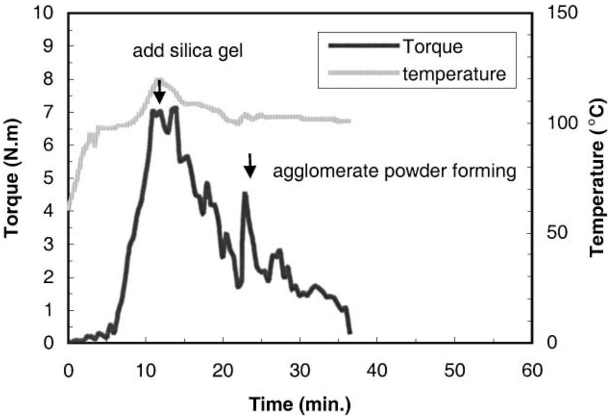


*Figure 3* Variation of the mixer torque and emulsion temperature with time during the phase inversion emulsification of LDPE in the presence of 2% silica in the aqueous phase. Phase inversion from water-in-polymer melt to polymer melt-in-water resulted in a powder which could be dispersed into water. Aqueous phase fraction at phase inversion was $\phi^* = 0.29$.

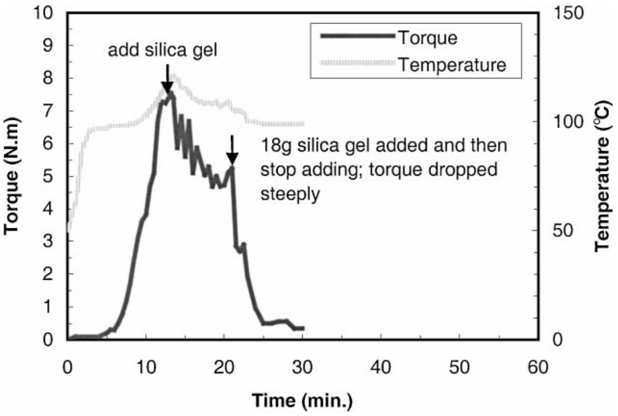


*Figure 4* Variation of mixer torque and emulsion temperature with time during the emulsification of LDPE melt in the presence of 5% silica in the aqueous phase. Due to the solidification of the melt, water could not be incorporated after adding 13% silica gel.

## 3. Results

### 3.1. Emulsification history–torque, temperature and time curves

Fig 1 shows the Torque, Temperature and Time curves when only pure water was added into the system without silica. The phase inversion from water-in-polymer melt to polymer melt-in-water occurred when 20% water (31 g) had been added into the system. Then the resulting emulsion was further diluted to contain 40% water.

Fig. 2 gives the corresponding result when silica (concentration of silica in water was 1%) was included in water. The period during which silica gel addition was suspended is also apparent in Fig. 2. The emulsion formed when 46 g silica gel had been added into the system. Silica gel addition was intermittent to allow the torque to recover and incorporate water into the polymer melt.

Fig. 3 indicates a different behaviour. In this experiment the silica gel (concentration of silica gel was 2%) was added into the system without interruption. The torque oscillated strongly. This is because this silica gel has high viscosity and aggregation of the gel strongly influences the viscosity of the mixture. Therefore, the rheological property represented by the torque showed large changes. Finally, after 50 g silica gel had been added, an agglomerated powder was obtained rather than an emulsion.

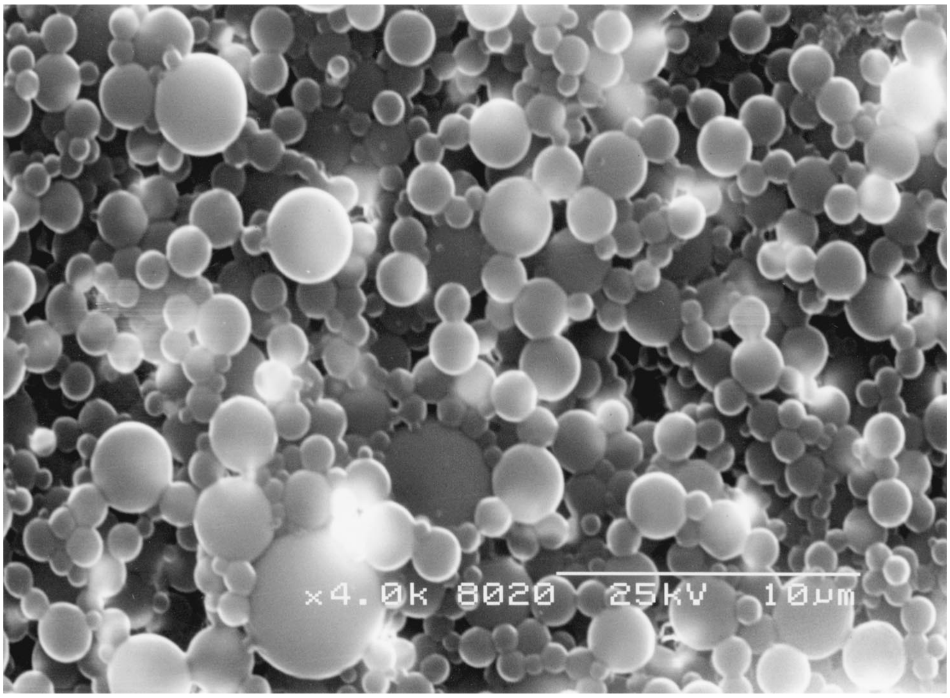
Fig. 4 shows the results obtained when high concentration silica gel (5%) which was added into the system. The torque suddenly dropped down to a low level after adding only 18 g silica gel. It was not possible to keep the torque high as no further water could be incorporated into the polymer which appeared to solidify. Therefore, no emulsion or powder could be obtained.

### 3.2. Morphology of dispersions

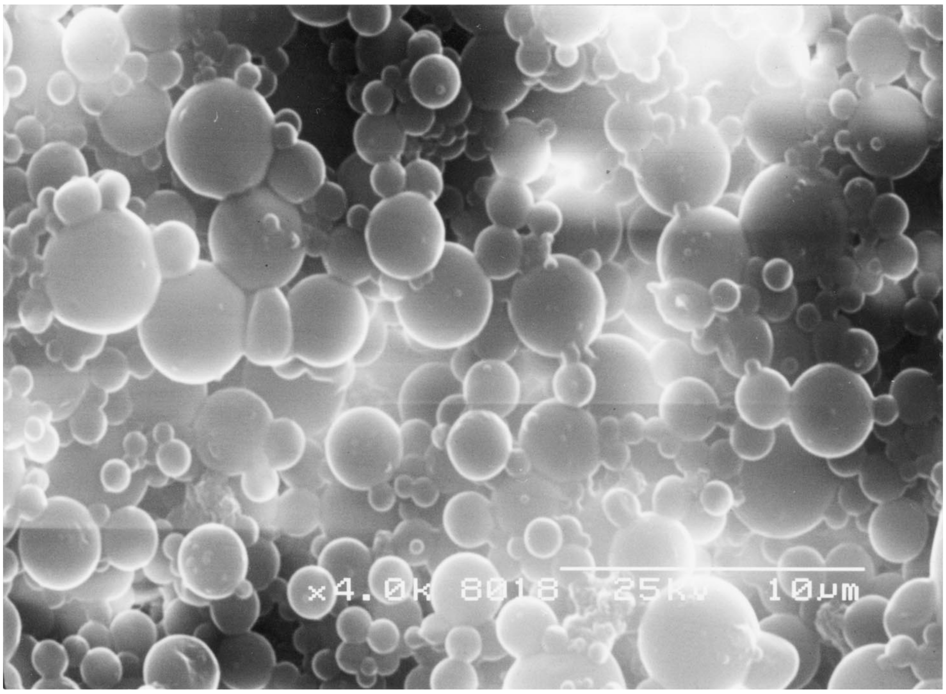
The morphology of the dispersions was examined by using scanning electron microscopy (SEM). The results are shown in Figs 5–7. Fig. 5a, b show the effect of silica concentration on emulsification products. As the silica concentration is increased, the particle size also increases, in confirmation with the particle size analysis by method 2.2.5. Fig. 6a, b illustrate the surface morphology of the films formed by the dispersions with or without silica, but without heat treatment. The particulate nature of the film is more pronounced when silica is present but there are no large aggregates present. Without silica, particles appear to aggregate more rapidly and extensively. When the films formed by the dispersions are heat treated at 135°C, their particulate nature disappears but the aggregate concentration is increased as shown in Fig. 7a, b. Nevertheless, there are less aggregates present when silica is present.

### 3.3. Environmental SEM and particle aggregation

As observed in Figs 8 and 9, the particle aggregation behaviour of the dispersions is different with or without silica. As water is evaporated from the samples during film formation, particle aggregation takes place and large flocks of ca. 7 $\mu$m are formed. The numbers of such flocks are substantially greater in the absence of silica as shown in Fig. 8a compared with Figs 8b and 9b in the presence of silica. Flock formation can be observed by using the Environmental Scanning Electron



(a)



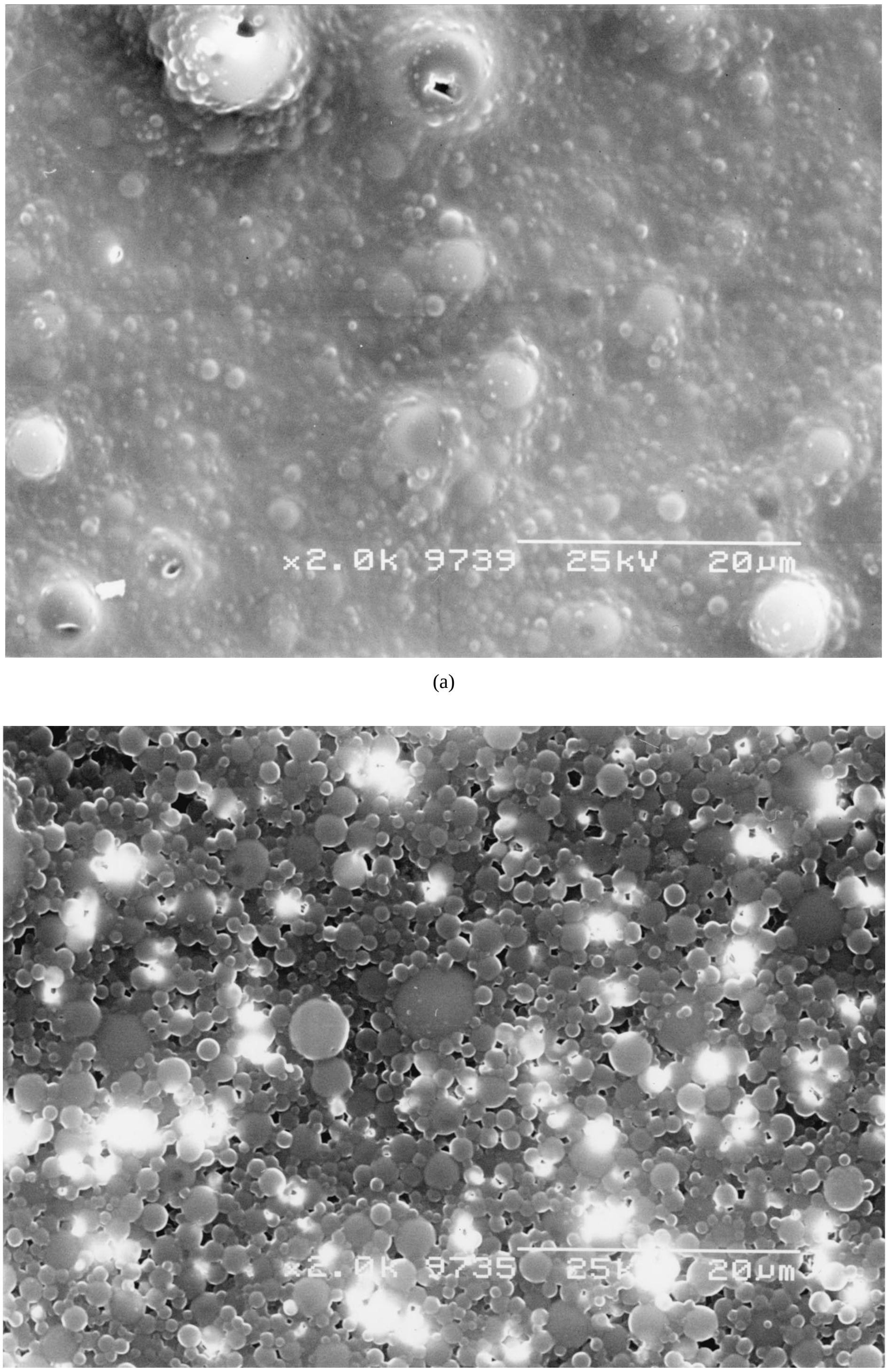
(b)

*Figure 5* (a). SEM micrograph of LDPE emulsified using 20% HMWSP (A-2) and silica gel (concentration 1%). (b). SEM micrograph of LDPE particles in an agglomerate powder form. It was obtained by using 20% HMWSP (A-2) and silica gel (concentration 2%). The average particle size of the agglomerate powder is bigger than the emulsion particles shown in (a).

Microscopy (E-SEM) when wet samples are viewed without coating. When the pressure in the electron microscope was reduced thus causing the evaporation of water, flock formation could be observed. In Fig. 8a, b, the E-SEM pressure is approximately 3.7 Torr (493 Pa). Already, large flocks are forming in the absence of silica (Fig. 8a) while no flock formation is apparent in the presence of silica (Fig. 8b). As the pressure is reduced further to 2.0 Torr (266 Pa), smaller numbers of flocks are present in the silica containing emulsion (compare Fig. 9a and 9b). When the pressure is reduced to 1.4 Torr (186 Pa), flock formation is extensive as show in Fig. 10 when no silica is present. These results are in agreement with the SEM results as presented through Figs 5–7.

## 3.4. Crystallinity of films formed from LDPE emulsion

The results obtained from the diffractometer (X-ray) examination showed that crystallinity of the film with concentration 1% silica gel is 23% and the film which was without silica is 25%. This difference is probably



(a)

(b)

*Figure 6* SEM micrographs showing the surface morphology of the films after drying at room temperature. The emulsion film was formed as a result of water evaporation and coalescence of the polymer particles. Film (a) was without silica and film (b) was with 1% silica in the aqueous phase.

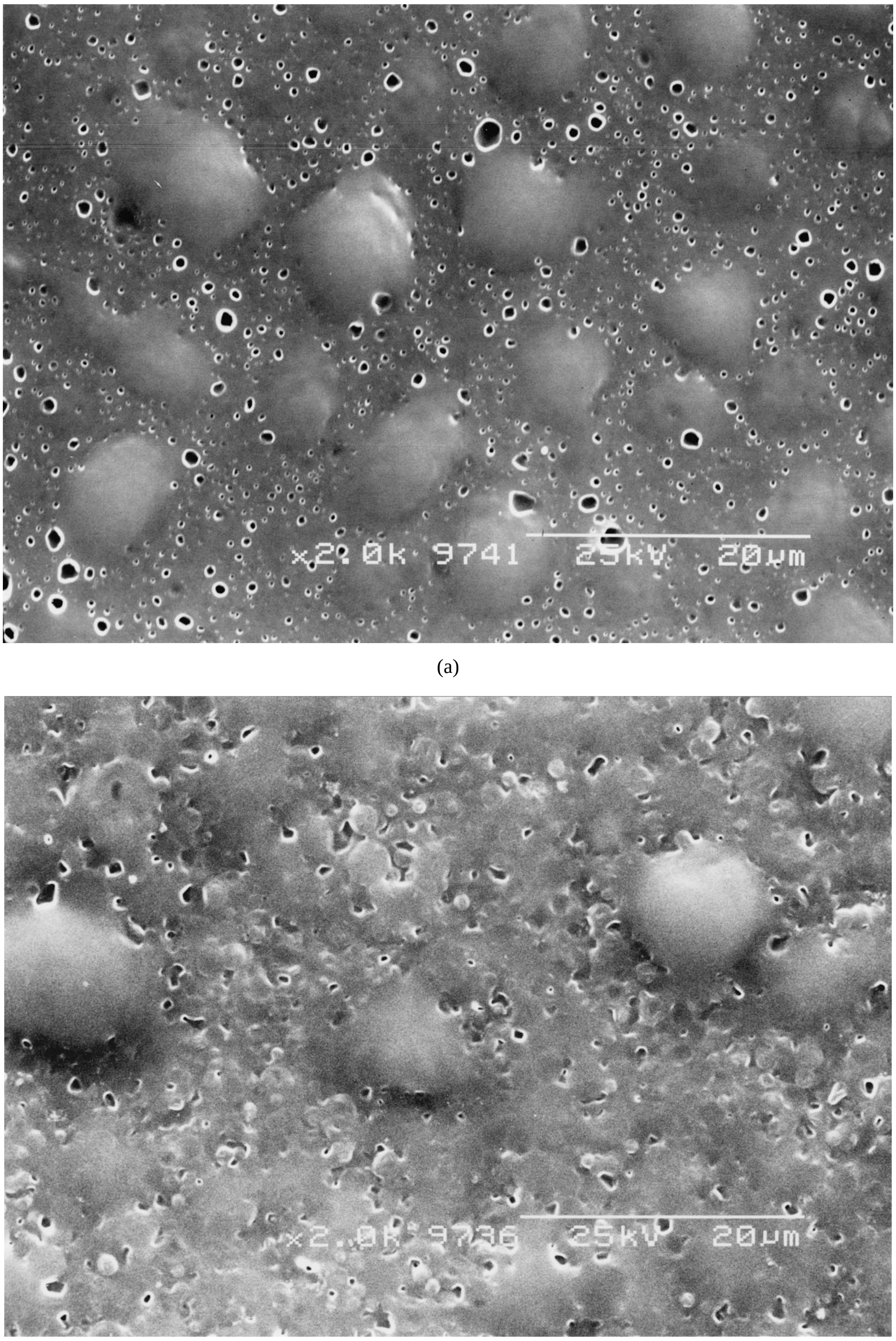
not significant although the trend is in agreement with the previous findings [6, 7]. The size of the crystals were estimated by using the Scherrer equation [20]:

$$t = \frac{k\lambda}{B\cos\theta}$$

where $t$ represents the extent of the crystal measured in the direction normal to the planes to which the diffraction peak corresponds. $k \cong 0.9$, a coefficient; $\lambda = 0.1542$ nm, the wavelength of Cu radiation; and $B$ the breadth of the peak at half peak height in radians and $\theta = 10.25^\circ$ is the Bragg angle. The peak breadth was $1^\circ \equiv \pi/180$ radians and the crystal size based on the Scherrer equation was found to be 8 nm.

### 3.5. Particle size analysis and emulsion stability

Particle size analysis of the powdered LDPE dispersions was performed after dispersing them in water. The results are shown in Table I.



(a)

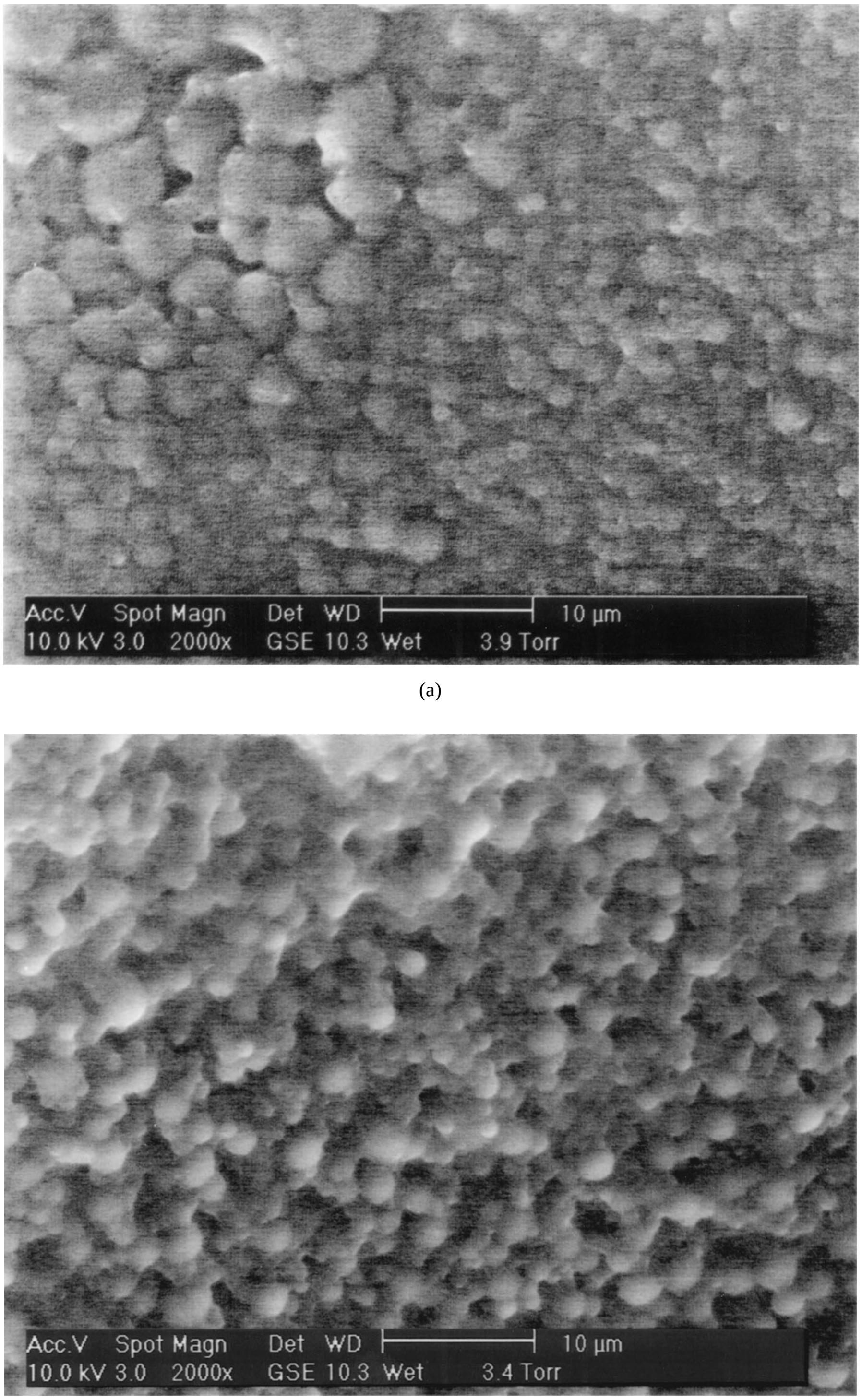
(b)

*Figure 7* SEM micrographs of the same films as in Fig. 6, but after curing the films at 135°C for 30 minutes and cooling down to room temperature in 4 hours from 135°C. (a) no silica, and (b) 1% silica in aqueous phase.

TABLE I The particle size and distribution

| Materials | Silica % | Span | $D$ $\mu$m <br> $D$ [4, 3] | <br> $D$ [3, 2] | <br> $D[v,0.9]$ | <br> $D[v,0.1]$ | <br> $D[v,0.5]$ |
|---|---|---|---|---|---|---|---|
| LDPE + A-2 | 0.0 | 1.75 | 1.22 | 0.80 | 2.22 | 0.42 | 1.03 |
| LDPE + A-2 + Silica | 1.0 | 6.34 | 5.71 | 1.08 | 9.56 | 0.52 | 1.43 |
| LDPE + A-2 + Silica | 2.0 | 22.9 | 12.09 | 1.54 | 47.6 | 0.68 | 2.05 |

As seen from Table I, the volume average particle size $D$ [4, 3] increases significantly in the presence of silica. However, the increase in the surface average particle size $D$ [3, 2] and in particle size at 50% cumulative $D[v,0.5]$ are not as significant. When the silica concentration in the aqueous phase is 2%, the increases in $D$ [4, 3], $D$ [3, 2] and $D[v,0.5]$ are very large compared with the no silica sample. This is due to the fact that



(a)

(b)

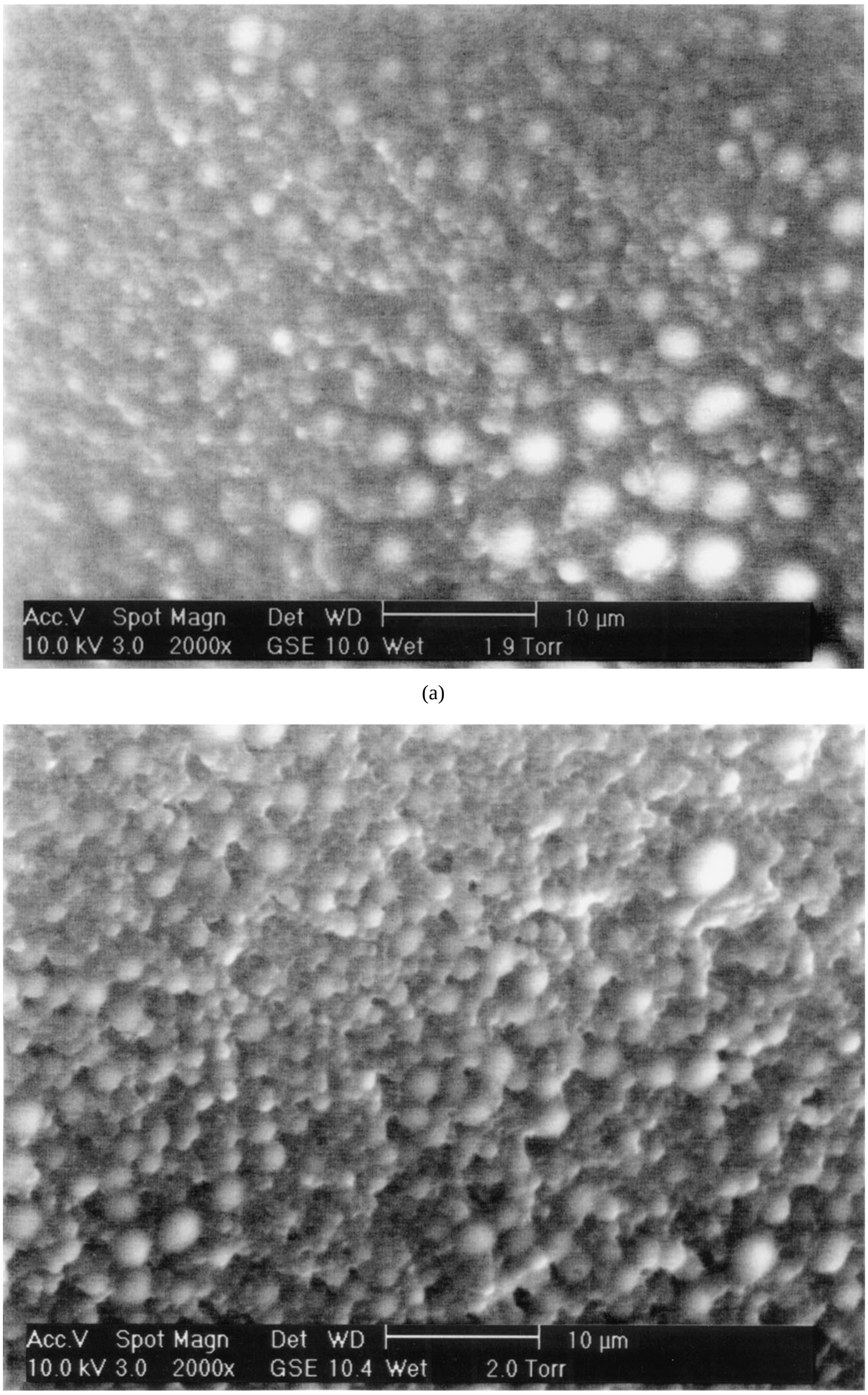
*Figure 8* Environmental SEM micrographs of LDPE dispersions at pressure of 3.4 Torr (452 Pa), (a) dispersion with no silica, (b) dispersion with 1% silica in the aqueous phase.

in this case a powder is obtained and it is subsequently dispersed into water. If the distribution conditions were mild (i.e. ultrasound was not used) we could expect incomplete aggregate break-up. The broadening of the particle size distribution as a result of silica addition is neglected in the increase of particle size span. The physical state of dispersions after 8 weeks of emulsification is evaluated in Table II.

It was found that in the absence of silica, a hard skin was formed with the emulsion having a high viscosity. In the presence of silica, the thickness of the skin and viscosity of emulsions were low.

## 3.6. The effect of silica on emulsion viscosity

Fig. 11 illustrates the variation of the dispersion viscosity with shear rate. The dispersions contained 40% water. In the presence of silica, low shear rate viscosity is reduced while the high shear rate viscosity is slightly



(a)

(b)

*Figure 9* Environmental SEM micrographs of LDPE dispersion is at pressure of ∼2.0 Torr (266 Pa). Sample identification is as same in Fig. 8.

higher compared with the no silica case. The shear thinning ability of the dispersion is also reduced in the presence of silica. These results can be explained in terms of particle size distribution [2] which is broader when silica is used.

## 4. Discussion

When the silica dispersion is added into the polymer melt containing surface active material (HMWSP), we can assume that the displacement of water from silica starts initially through the adsorption of HMWSPs onto the silica surface. As the silica surface becomes more hydrophobic, LDPE chains also start attaching onto the silica as a result of flow induced diffusion during mixing [6, 7]. The incorporation of silica into polymer not only releases water but also increases the effective melting temperature as well as its viscosity [6, 7]. As a result, phase inversion from a water-in-polymer melt to polymer melt-in-water takes place. If the concentration of silica in water is very high (5%) the increases in viscosity and polymer melting temperature are more marked and the incorporation of water becomes more difficult and therefore complete phase separation takes place.

The Environmental SEM and conventional SEM studies indicate that the coalescence behaviour of the

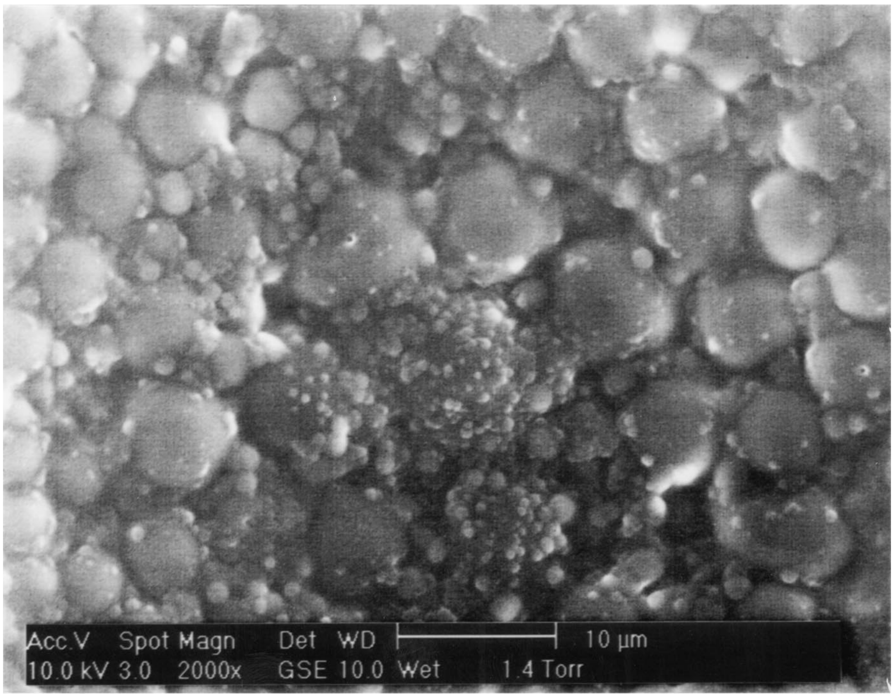


*Figure 10* Environmental SEM micrograph of LDPE dispersion containing no silica when the pressure is 1.4 Torr (186 Pa).

TABLE II The stability of emulsion

| Materials | Silica % | Hard skin | Fluidity |
|---|---|---|---|
| LDPE + A-2 | 0.0 | Formed hard skin which thickens with time | Underneath skin, material can flow but was high viscosity |
| LDPE + A-2 + Silica | 1.0 | Thin hard skin | Good fluidity |
| LDPE + A-2 + Silica | 2.0 | Agglomerated spherical powder | No fluidity but disperses well in water |

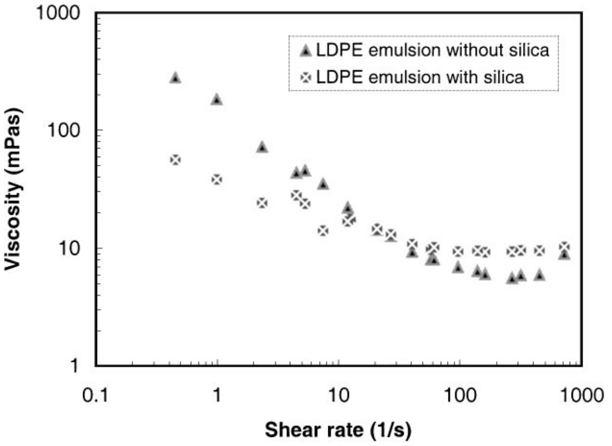


*Figure 11* The effect of silica on the shear rate dependent viscosity of the LDPE dispersions.

polymer dispersions with or without silica was significantly different. Large numbers of flocks were formed when there was no silica present, while the number of such flocks was substantially reduced when silica was present. Therefore, the samples with silica form smoother films. The process of coalescence was clearly observed under Environmental SEM as water was evaporated from the dispersions. This difference between the coalescence behaviour can be explained by the interfacial conformation of the HMWSPs. In the absence of silica, HMWSPs on the surface of the LDPE particles and in the aqueous phase will cause bridging through hydrophilic tails as water is evaporated. In the presence of silica, these tails will interact with silica particles and therefore the interfacial area between the interacting tails will be reduced thus preventing coalescence. It must be noted that we would have expected more coalescence in samples with larger particles and broader particle size distribution as in the case of silica-containing dispersions.

As a result of particle coalescence during the film forming process, polymer films containing no silica were not smooth. Such films could be heat treated (curing) to form a smooth, continuous film. However, if the curing temperature was low (say 135°C as in the present case), the particulate nature of the films was still present as shown in Fig. 7. In both cases, the particulate nature of the films disappeared when the films were cured at 150°C. However, their transport properties against gases and solvents might be different.

As seen in Fig. 7, there are several defects present on the surface of the films. These were due to the rapid evaporation of water during film formation. These defects were less marked if the viscosity of the dispersion was low as in the case of silica containing dispersion (Fig. 7). The viscosity of the dispersion with silica was lower at low shear rates compared with the emulsion with no silica. Furthermore, the silica containing dispersion was less shear thinning. These viscosity characteristics are the direct result of the particle size distribution in these dispersions in which the silica-containing dispersions have a broader distribution.

The dynamics of film formation in these dispersions were investigated using an Environmental SEM which indicated that during the evaporation of water, the particle coalescence was significantly more extensive when the dispersion did not contain any silica. SEM studies confirmed these findings. It was suggested that the presence of extensive coalescence was due to the particle bridging by the hydrophobically modified water soluble polymers on the polymer particles and in water. Due to the adsorption of HMWSPs on the silica surface through the ionic side chains, the bridging by the HMWSPs was reduced in silica containing dispersions.

## 5. Conclusions

Low density polyethylene (LDPE) melts were emulsified in water and subsequently cooled to obtain colloidal dispersions, by flow induced phase inversion emulsification method. Hydrophobically Modified Water Soluble Polymers (HMWSPs) were used as surface active material for emulsification. Hydrophilic silica (particle size 7 nm) in the aqueous phase was used to modify the film forming characteristics of the dispersion. It was shown that the presence of silica in the aqueous phase (1%) increased the phase volume of water at phase inversion from a water-in-polymer melt to polymer melt-in-water emulsion. This was due to increased viscosity of the aqueous phase in the presence of silica. It was suggested that, during the water-in-polymer melt emulsification stage, the surfaces of the silica particles were covered by HMWSPs initially and then followed by coverage with LDPE. Consequently, the transfer of silica from the aqueous phase to the polymer melt phase resulted in viscosity decrease in the aqueous phase and viscosity increase in the polymer phase, thus leading to phase inversion. When the amount of silica in water was increased to 2%, a powdery dispersion was obtained which could be dispersed into water readily. If the amount of silica was too high (5%), due to very rapid change in the viscosity ratio of the phases, water could not be incorporated into the polymer melt and thus the emulsion could not be obtained. The dispersions with silica appear to form a more uniform film. Powdery dispersions obtained in the presence of silica can be used in the powder coating applications.

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## References

1. G. AKAY and LI TONG, *J. Colloid Intrf. Sci.*, submitted.
2. G. AKAY, *Chem. Eng. Sci.* **53** (1998) 203.
3. *Idem.*, *European Patent* 649867 (2000).
4. G. AKAY and LI TONG, *Chem. Eng. Tech.* **23** (2000) 285.
5. G. AKAY, A. KAZEEM, S. Y. CHEN and R. A. CHOUDHERY, "Recent Advances in Particle Technology" (IChemE, UK, 1998) CD-Rom.
6. G. AKAY, *Polym. Eng. Sci.* **30** (1990) 1361.
7. *Idem.*, *ibid.* **34** (1994) 865.
8. M. KAWAGUCHI, A. MIZUTANI, Y. MATSUSHITA and T. KATO, *Langmuir* **13** (1997) 6339.
9. E. BOURGEATLAMI, P. ESPIARD, A. GUYOT, C. GAUTHIER, L. DAVID and G. VIGIER, *Angew. Makromol. Chemie* **242** (1996) 105.
10. P. M. DOVE and J. D. RIMSTIDT, in "Silica," edited by P. J. Heaney, C. T. Prewitt and G. V. Gibbs (Washington DC-Mineralogical Society of America, 1994) p. 259. Reviews in Mineralogy Vol. 29.
11. R. K. ILER, "The Colloid Chemistry of Silica and Silicates" (Cornell University Press, New York, 1955).
12. *Idem.*, "The Chemistry of Silica" (A Wiley-Interscience Publication, New York, 1979).
13. C. AMIEL, M. SIKKA, J. W. JR. SCHNEIDER, Y. TSAO, M. TIRRELL and J. W. MAYS, *Macromolecules* **28** (1995) 3125.
14. G. AKAY, in "Polymer Powder Technology," edited by M. Narkis and N. Rozenweig (Wiley, New York, 1998) p. 541.
15. *Idem.*, US Patent 4 988 369(1991), European Patent 307 278 (1992) and Japanese Patent 94037634 (1994).
16. G. AKAY, V. J. PRICE and S. Y. CHEN, in "Recent Advances in Particle Technology" (IChemE, UK, 1998) CD-Rom.
17. B. R. MIDMORE, *Colloids and Surfaces A-Physicochemical and Engineering Aspects* **132** (1998) 257.
18. S. R. RAGHAVAN, M. W. RILEY, P. S. FEDKIW and S. A. KHAN, *Chem. Mater.* **10** (1998) 244.
19. G. AKAY and R. J. WAKEMAN, *J. Membr. Sci.* **131** (1997) 229.
20. D. CAMPBELL and J. R. WHITE, "Polymer Characterization" (Chapman and Hall, New York, 1989).

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