Colloid Polym Sci 279:1118–1125 (2001)
© Springer-Verlag 2001

ORIGINAL CONTRIBUTION

G. Akay
L. Tong
M. J. Hounslow
A. S. Burbidge

Intensive agglomeration and microencapsulation of powders

Received: 15 December 2000
Accepted: 24 April 2001

G. Akay (✉) · L. Tong
Process Intensification and
Innovation Centre
Department of Chemical and
Process Engineering
University of Newcastle
Newcastle upon Tyne NE1 7RU, UK
e-mail: galip.akay@newcastle.ac.uk
Tel.: +44-191-2227269
Fax: +44-191-2225292

M. J. Hounslow
Department of Chemical and
Process Engineering
University of Sheffield
Sheffield, S1 3JD, UK

A. S. Burbidge
School of Chemical Engineering
University of Birmingham
Birmingham B15 2TT, UK

Abstract Highly concentrated colloidal latex particles from thermoplastics (low-density polyethylene) can be obtained by using phase-inversion emulsification of a polymer melt in which hydrophobically modified water-soluble polymers are used to provide surface activity. Initially, a water-in-polymer-melt emulsion is obtained and subsequently inverted to a polymer-melt-in-water emulsion when a critical aqueous phase volume is reached. After the phase inversion and subsequent dilution of the emulsion, if the solidification of the melt is carried out during mixing, another phase inversion takes place and water-in-solid-polymer aggregates are formed even if the phase volume of the aqueous phase is well above the critical value. These aggregates contain an aqueous phase encapsulated by the polymer. The kinetics of this phase inversion is studied and the use of the technique to obtain microcapsules from aqueous solutions is investigated.

Key words Agglomeration · Emulsification · Microencapsulation · Phase inversion · Process intensification

Introduction

Thermoplastic powders based on high-molecular-weight polymers that exhibit excellent chemical resistance, toughness and flexibility can be used in powder coating; however, thermoplastics, such as polyethylene, polypropylene, nylon, poly(vinyl chloride) and polyesters, tend to be difficult to grind down to obtain uniform fine particles. This restricts the thickness of the coatings based on these powders to 30–60 μm or greater [1]. In the late 1980s, Tanaka and Honma [2] employed an extruder and a complex surfactant system to obtain a thermoplastic aqueous powdery dispersion.

Recently, we have investigated the fundamental processes involved in the emulsification of polymeric resins [3–5] and thermoplastics [6–8] using the so-called flow-induced phase-inversion (FIPI) phenomenon [3, 4, 9]. The FIPI phenomenon has been applied to the intensive processing of structured materials (intensive structuring) including emulsification [3–8], agglomeration and microencapsulation [9–15], preparation of microporous polymers [16] and inversion of lamellar liquid-crystal phases to multilamellar droplet dispersions [17]. In particular, the effects of flow field, surfactant system and the molecular characteristics of the polymeric surface-active materials on the dynamics of emulsification and the emulsion characteristics have been studied [3–9]. The emulsification of such highly viscous materials in water requires a phase-inversion technique from an initial water-in-oil to a final oil-in-water emulsion. Here, oil is either a viscous polymeric resin or a polymer melt. We have shown that molecular

surfactants could not be used in the emulsification of polymer melts in water and that polymeric surfactants with certain restrictions on their molecular structure had to be used [7, 9]. The emulsification of the polymeric resins and thermoplastics could be intensified by using the FIPI technique [3–9], which also yielded colloidal emulsions with a narrow size distribution. Depending on the thermodynamic conditions (such as surfactant system, oil-phase viscosity, temperature and phase volume of the aqueous phase), phase inversion takes place at a critical deformation rate. In order to reduce the particle size and the spread of the particle size distribution (particle size span), the FIPI needs to be carried out at deformation rates well above the critical deformation rate. It was shown that as the viscosity of the oil phase approaches about 1000 Pas the phase volume of the aqueous phase approaches about 0.2, indicating that the particles are in a close-packed state.

In the emulsification of thermoplastics, after the phase inversion from a water-in-polymer-melt to a polymer-melt-in-water emulsion, the polymer melt droplets need to be solidified to obtain a polymer-latex-in-water dispersion. In obtaining the polymer latex particles from the polymer-melt-in-water emulsion, the polymer melt is solidified, which when carried out under static conditions yields concentrated polymer latexes; however, if the solidification is carried out while mixing, a new thermomechanically induced phase inversion takes place even if the phase volume of the aqueous phase is well above 20%. In this study we explore further this new thermomechanically induced phase inversion and apply it to the encapsulation of particles in the presence of an aqueous phase. The incorporation of active ingredients in the presence of water into the polymeric coat to obtain microcapsules will be difficult without a phase-inversion stage. Phase reinversion from a polymer-melt-in-water to a water-in-solid-polymer dispersion (microcapsules) ensures that a uniform coating is present around the aqueous phase droplets. However, in this initial study, we only use water to obtain powdered aggregates in which water is encapsulated by a thermoplastic (low-density polyethylene, LDPE).

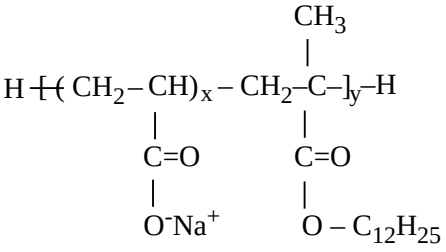
In order to obtain free-flowing microcapsules, it is possible to combine the so called FIPI agglomeration/microencapsulation techniques [9–15] with the present method by incorporating solid particles into the polymer, either as an active ingredient or as a surface modifier. FIPI microencapsulation of liquids (silicone fluid) in the presence of solids (as a carrier for the liquid) has already been performed [9–15].

In this study, we explore the dynamics of the thermomechanically induced phase inversions and discuss their applications in the microencapsulation of actives in the presence of an aqueous phase. FIPI based processes represent process intensification when these processes are carried out at very high deformation rates [4–10].

Experimental

Materials

LDPE was supplied by Exxon, coded LD655, with $M_n = 40{,}000$ and density 920 kg/m^3. The surfactant (coded A2) was a hydrophobically modified water-soluble polymer (HMWSP) based on poly(acrylic acid) sodium salt and supplied by National Starch and Chemical Company. This was in the form of 25% solid by weight in water and the solution pH was 4.2. This surface-active material was coded HMWSP-A2 in our previous studies [7, 8]. Its chemical structure is as follows [7, 8, 18, 19]:



Here, $x = 8$ and $y = 3$. These HMWSPs are used as viscosity modifiers, as well as stabilizers for dispersions [16–18].

The fumed hydrophilic silica powder, Aerosil 380, was supplied by Degussa. The average primary particle diameter was 7 nm and the surface area was 380 m^2/g. Owing to its very high surface area, silica has been used to cause phase inversion in FIPI agglomeration and microencapsulation processes [10, 13].

Equipment

Haake high-torque mixer

Emulsions were prepared using a high-torque-process rheometer (Haake Rheocord 9000) fitted with an internal mixer. The Rheocord 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 a 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. During the experiment the temperature of the mixer can be controlled using an air cooling system. The torque on the rotors, the change in temperature and the speed of the rotor are recorded as functions of time; therefore, the full phase-inversion history can be profiled. In the experiments reported here a constant rotor speed (60 rpm) was used. The torque data are expected to give an insight into the phase inversion during mixing. The structuring process can be monitored by recording the variation of the torque and the temperature of the mixer.

Scanning electron microscopy

Aggregation and morphology studies of LDPE powders were conducted using a Hitachi S-2400 scanning electron microscope (SEM). LDPE powder samples containing water were fractured in liquid nitrogen then stuck onto SEM specimen stubs using double-sided conductive adhesive tape and the samples were carbon-coated prior to observation. Before the carbon coating, water was evaporated under vacuum.

Particle size and size distribution analysis

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

$$S = (D[v,0.9] - D[v,0.1])/D[v,0.5] \ ,$$

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 were computed using the software available in the Malvern Mastersizer.

Differential scanning calorimetry

Differential scanning calorimetry (DSC, Mettler FP90) was used to measure the thermal properties of the polymers using heating and cooling programmes. It was used to evaluate the LDPE crystal melting behaviour and recrystallisation. The thermal characteristics are very important and relate to the phase reinversion occurring during the cooling process. The heating/cooling rate used was 10 °C/min.

LDPE dispersion preparation

LDPE granules (100 g) and of HMWSP-A2 solution (100 g, containing 25 wt% surfactant and 75 wt% water) were mixed together in a beaker. The mixer was set to heat up to 120 °C and when the temperature reached 60 °C the rotors were turned on (60 rpm) and the mixture added. The torque was very low at the beginning because of the high water content. As the 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 at room temperature was titrated into the LDPE/HMWSP-A2 blend. 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 pure water was about 1.5 g/min. During water addition, the temperature fell as well but, owing to the low addition rate, it was kept above the LDPE crystal melting temperature of 102 °C. When the water concentration reached a certain critical value, a LDPE-melt-in-water emulsion was formed. Water addition was continued until the phase volume of the aqueous phase reached the desired value. Afterwards, the temperature was reduced to 45 or 60 °C while the mixing continued at constant speed. The phase reinversion occurred during the cooling process. The phase reinversion characteristics of the LDPE and A2 melt with different water contents were recorded.

Results and discussion

Recrystallisation of LDPE

LDPE is a semicrystalline polymer. The recrystallisation takes place when the LDPE is cooling from the melt. As recrystallisation is an exothermic reaction, there is a sharp DSC signal to indicate this phase transition Fig. 1.

Two samples, pure LDPE and LDPE latex dispersion, were prepared. The pure LDPE was from LDPE granules. The LDPE latex dispersion (obtained after the first phase inversion) had HMWSP (macromolecular surfactant: HMWSP-A2). Water was evaporated from the aqueous dispersion at room temperature under vacuum. The DSC measurements yield the crystallisation temperature peak, T_{pc}, and the enthalpy of this phase transition, ΔH_c, for pure LDPE and the mixture of LDPE with HMWSP-A2. From the DSC data we observe that for pure LDPE $T_{pc} = 86.3$ °C and $\Delta H_c = 14.0$ J/g; while for the LDPE/HMWSP-A2 blend $T_{pc} = 92.9$ °C and $\Delta H_c = 7.17$ J/g. The reduction in the enthalpy of crystallisation indicates that the LDPE/HMWSP-A2 blends are less crystalline and that the increase in the peak crystallisation temperature is a result of the polyelectrolyte nature of the macromolecular surfactant HMWSP-A2. The information given by the DSC test is very important in the setting of the experimental conditions and in the understanding of the phase reinversion process.

Phase inversions

The typical variation of the mixer torque as a function of time during the emulsification of the LDPE/HMWSP-A2/water system is shown in Fig. 2. This figure illustrates the presence of two phase inversions; the first inversion takes place under isothermal conditions, while the second inversion occurs during cooling. After each phase inversion, the structures of the particulate systems obtained are very different and, therefore, can be utilised for a particular purpose. In the following, we illustrate the history and the characteristics of these phase inversions.

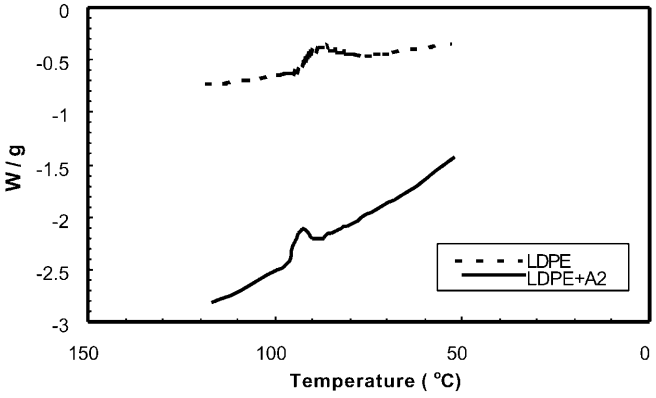


Fig. 1 Differential scanning calorimetry results for low-density polyethylene (*LDPE*) and LDPE/hydrophobically modified water-soluble polymer surfactant (*HMWSP-A2*) dispersion (after the evaporation of water) during the cooling cycle. The cooling rate was 10 °C/min

First phase inversion and formation of the polymer-melt-in-water emulsion

In Fig. 2, the first peak in the torque essentially represents the mixing of the LDPE with the macromolecular surfactant HMWSP-A2. When the temperature reaches 120 °C above the melting point of the LDPE, the mixer torque becomes very high but relatively stable. In this experiment, water addition was started immediately after reaching the maximum torque. It was shown that the excessive mixing of the polymer with the macromolecular surfactant results in the loss of surface activity [8] as the surfactant formed aggregates dispersed in the LDPE melt. Initially, the macromolecular surfactant forms the continuous phase in the LDPE melt/macromolecular surfactant system. When the aqueous phase is titrated (at a rate of 1.5 g/min), the mixer torque drops suddenly since the incorporation of water into the polymer melt is not very rapid owing to the very high viscosity of the continuous LDPE melt phase. Rapid inclusion of water into the polymer melt can be achieved by using purpose-built equipment [3, 4, 19]. During this period, a water-in-polymer-melt emulsion is formed.

When the phase volume of the aqueous phase reaches 20%, phase inversion from a water-in-polymer-melt] to a polymer-melt-in-water emulsion takes place. This phase inversion can be detected by the increase in the torque and the temperature as seen in Fig. 2. The increase in torque, despite an increase in temperature, is a result of the presence of a co-continuous state during phase inversion [4]. When the phase inversion is complete, the torque is reduced and becomes steady. The temperature increase during phase inversion is the result of better thermal conduction when water becomes the continuous phase. We also observe a volume increase during the phase inversion, similar to the volume increase during the FIPI agglomeration [9–15].

Although the emulsion is colloidal in nature with a narrow size distribution, further reduction in the size and particle size span can be achieved if the phase inversion is carried out under higher deformation rates [3, 4].

After the first phase inversion to obtain a polymer-melt-in-water emulsion, the addition of water was continued to obtain the desired level of the aqueous phase in the emulsion while keeping the temperature at 100 °C. In the present case, the final aqueous phase volume was 20% (no dilution) to 40%.

After the first phase inversion and subsequent dilution, samples were taken from the LDPE-melt-in-water emulsion and were allowed to cool without mixing. The particle size and its distribution were analysed as a function of the macromolecular surfactant concentration. It was found that the surface average $D[3,2]$ and volume average $D[4,3]$ particle size, as well as the particle size span, all decrease with increasing macromolecular surfactant concentration until the concentration reaches 20% (by weight). Thereafter, these values appear to increase in general [8]; therefore, we used 20% surfactant in all the subsequent studies.

Second phase inversion

Preparation of water-in-solid-polymer agglomerates. After the formation of the LDPE-melt-in-water emulsion following the first phase inversion and subsequent dilution (if desired) a second phase inversion was observed if the cooling process was conducted while mixing as shown in Figs. 2 and 3. The history of the second phase inversion in which the cooling from 100 to 60 °C was conducted during the solidification of the LDPE melt. The onset and completion of the second phase inversion can be identified from the peaks in the mixer torque as shown in Figs. 2 and 3.

The second phase inversion starts when the temperature is reduced to about 92–93 °C. This temperature is close to the LDPE dispersion peak crystallisation temperature as indicated by the DSC data given in Fig. 3 for the 80% LDPE/20% A2 blend. The phase inversion proceeds for several minutes as indicated by

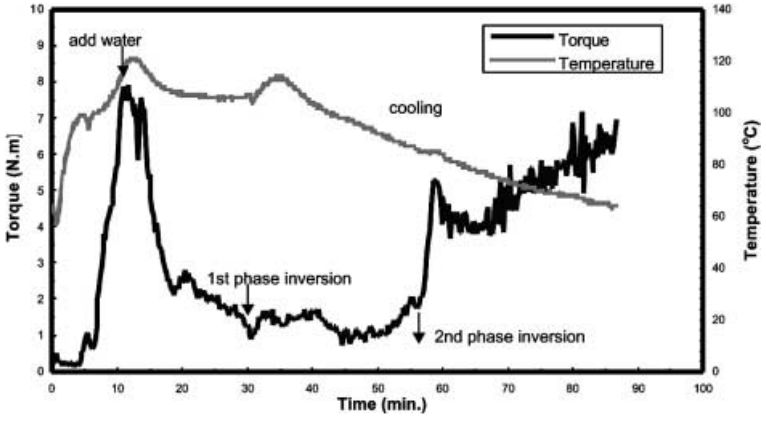


Fig. 2 Phase inversion emulsification history of the (80% LDPE/20% HMWSP-A2)/20% water system during the first and second phase inversions giving a polymer-melt-in-water emulsion and a water-in-solid-polymer dispersion (powdery dispersion), respectively

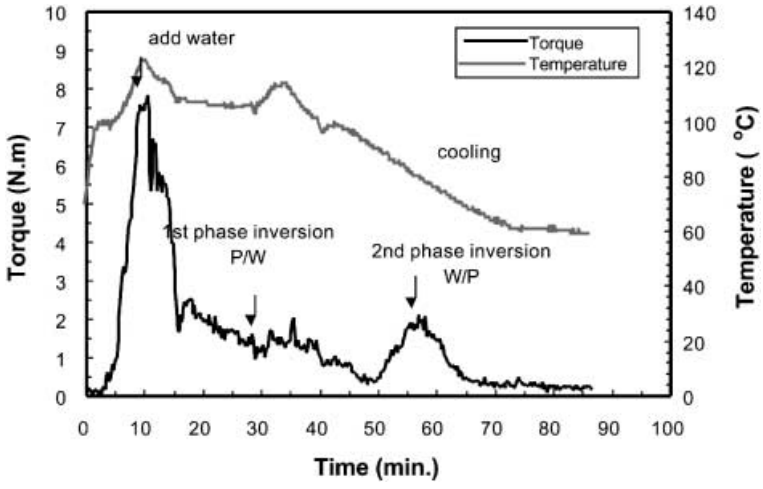


Fig. 3 Phase inversion emulsification history of the (80% LDPE/20% HMWSP-A2)/30% water system during the first and second phase inversions giving a polymer-melt-in-water emulsion and a water-in-solid-polymer dispersion (powdery dispersion), respectively. The first phase inversion takes place after the addition of 20% water and the polymer-melt-in-water emulsion is diluted to 30% water

the increasing torque until it reaches a steady state. The behaviour of the dispersion during the second phase inversion containing 20% water during the second phase inversion (Fig. 2) is somewhat different than the others, where the sustained mixing results in a further increase in the torque. However, when the aqueous phase volume is 25% or more (phase volume of water in Fig. 3 is 30%), there is a reduction in the torque after the initial rise and the powdery dispersion behaves more like a dry powder.

Recrystallisation is an exothermic process, and there is some evidence in Figs. 2 and 3 to indicate a small temperature rise caused by the enthalpy of crystallisation, ΔH_c; however, this increase is only small (as expected from the DSC data) and is only detectable when the water content of the dispersion is small.

The water content of these agglomerates was also measured by evaporation of the encapsulated aqueous phase under vacuum at 80 °C. It was found that they contain some 6% less water than expected on the basis of the added water; therefore, in the subsequent experiments, the amount of water was increased to compensate for the loss of water by evaporation during processing.

The effect of water phase volume on particle size. The effect of the water-phase volume in the water-in-solid-polymer dispersion on the particle size of the aggregates

Table 1 Particle size analysis of water-in-solid-polymer aggregates (powdery dispersion) with different water content obtained after the second phase inversion

Water content (%)	Span	D (μm)				
		D[4,3]	D[3,2]	D[v,0.9]	D[v,0.1]	D[v,0.5]
20	2.31	24.77	4.90	51.74	2.75	21.16
30	3.85	19.88	2.77	52.37	1.05	13.34

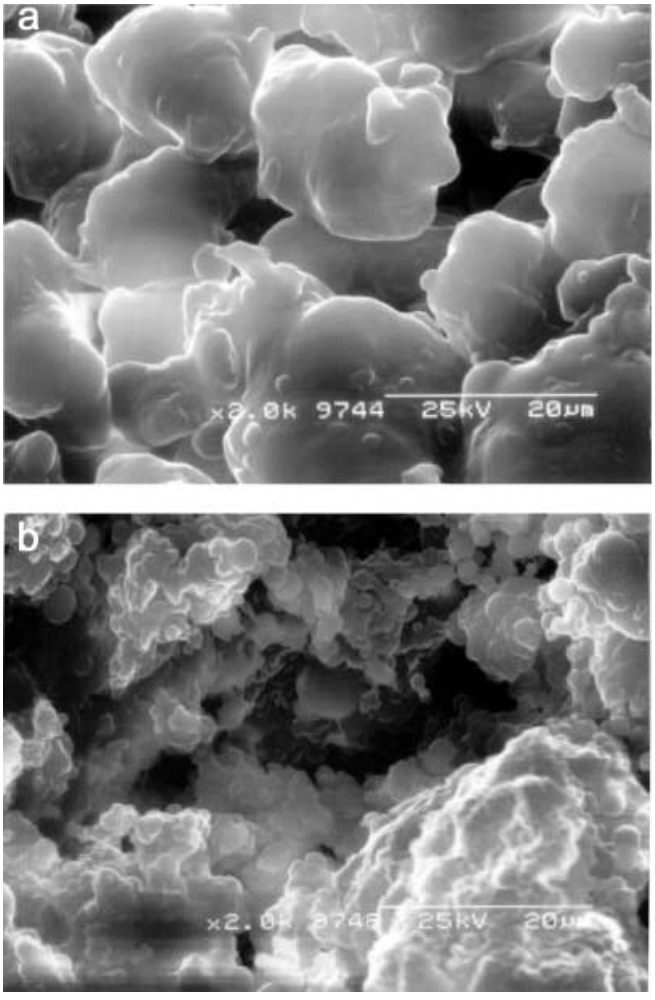


Fig. 4 Scanning electron microscopy (*SEM*) micrograph of water-in-solid-polymer aggregates containing **a** 20% and **b** 30% water, which is evaporated under vacuum before the SEM examination. In both micrographs the *scale bar* is 20 μm

is illustrated in Table 1. For this purpose, the water-in-solid-polymer emulsion was dispersed in water at room temperature and the particle size of the dispersion was measured. The particles that are measured are aggregates formed after the second phase inversion. It can be seen that the aggregate size decreases with increasing water-phase volume, in agreement with our qualitative observations that the higher the water-phase volume, the smaller the aggregate size and the more powder-like the behaviour, which is also apparent in the steady-state torque values in Figs. 2 and 3.

Morphology of aggregates. The morphology of the water-in-solid-polymer aggregates (powders) obtained after the second phase inversion is shown in Fig. 4. The primary particles forming the aggregated particles are smaller and more spherical in shape in Fig. 4b (water content 30%) than in Fig. 4a, where the water content is 20%.

Improvement of the flow characteristics of the aggregates. In our previous studies, fine silica was used as a very effective agent to induce phase inversion [9–15] as well as to improve the surface properties and flow characteristics of powders [10–15] and latexes [7]. Since the flow characteristics of the water-in-solid-polymer agglomerates are rather poor (they have the consistency of a moist powder), for some applications their flow properties may have to be improved. In order to achieve this, we used silica powder.

Silica can be added after the first phase inversion but before the onset of the second phase inversion. Figure 5 illustrates the history of the formation of the water-in-solid-polymer aggregates in which the water content in the aggregates was 25%. Here, after the second phase inversion, 0.83 g (0.5%) silica powder was added to the water-in-solid-polymer aggregates (which contained 100 g LDPE and 25 g HMWSP) following the second phase inversion at 60 °C. Subsequently, the mixing was continued for 12 min. Figure 5 also illustrates the effect of the water content on the steady-state torque after the second phase inversion as discussed previously (cf. Figs. 2, 3, 5).

The effect of silica on the agglomerate morphology is shown in Fig. 6. It can be seen that if silica is added after the second phase inversion, the particles are more discrete (Fig. 6b) compared with agglomerates obtained when silica is added after the first phase inversion (Fig. 6a). Although not measured, the flow characteristic of the agglomerates in Fig. 6b is better than that of the agglomerates illustrated in Fig. 4a and b and Fig. 6a.

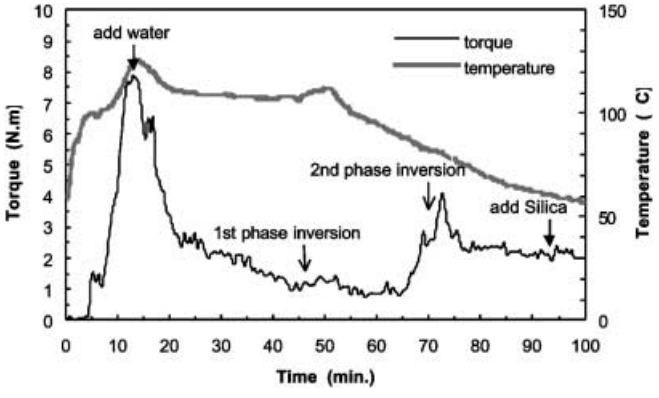


Fig. 5 Preparation of water-in-solid-polymer agglomerates in the presence of colloidal silica. The compositions and processing history were as follows. LDPE (100 g) and HMWSP-A2 (25 g) were mixed at 120 °C and 60 rpm followed by the addition of 25% water to obtain a LDPE-melt-in-water emulsion after the first phase inversion. The emulsion was cooled while mixing and after the second phase inversion water-in-solid-polymer aggregates were obtained. Then 0.83 g silica was added when the temperature was 60 °C. Cooling continued until the temperature was reduced to 50 °C

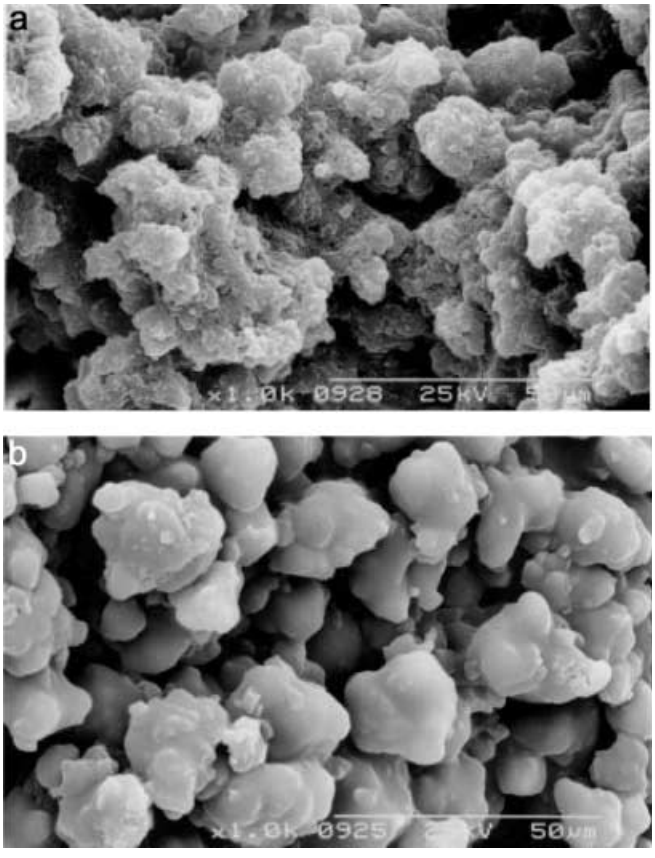


Fig. 6 Morphology of the water-in-solid-polymer agglomerates containing silica: **a** silica added after the first phase inversion but before the start of the second phase inversion; **b** silica added after the completion of the second phase inversion. In both micrographs the *scale bar* is 50 μm

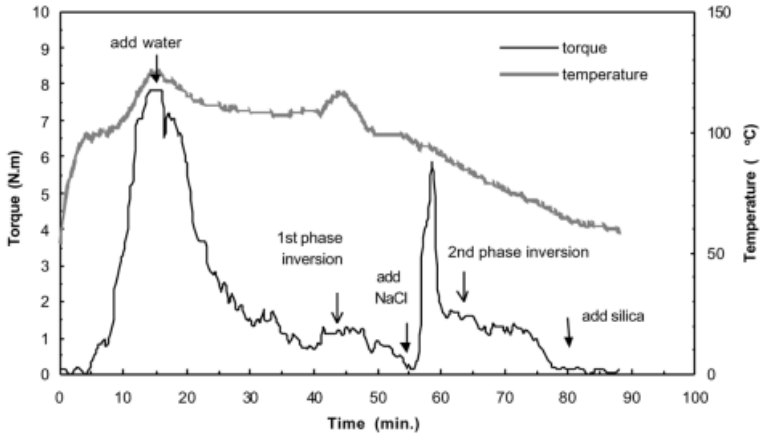


Fig. 7 Preparation of aqueous-phase-in-solid-polymer microcapsules in the presence of electrolyte (NaCl). The compositions and processing history were as follows. LDPE (100 g)and macromolecular surfactant A2 (25 g) were mixed at 120 °C and 60 rpm followed by the addition of 30% water to obtain a LDPE-melt-in-water emulsion after the first phase inversion. The emulsion was cooled while mixing and at 90 °C 18 g NaCl was added, which causes a rapid increase in torque, and water is separated from the emulsion particles, giving a clear solution. When the second phase inversion is complete, the aqueous phase is encapsulated by the solid polymer

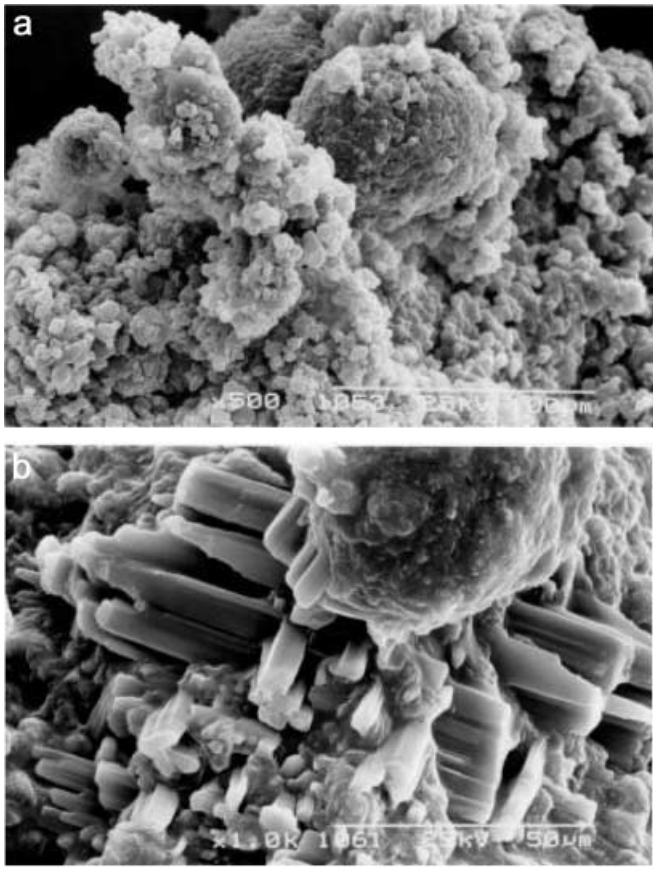


Fig. 8a, b SEM micrograph of aqueous-phase-in-solid-polymer microcapsules prepared using the technique described in the caption of Fig. 7. The aqueous phase contains 25 wt% electrolyte (NaCl). **a** No silica is added (*scale bar* = 100 μm); **b** microcapsules contain 0.5% hydrophilic silica (Aerosil 380) added after the completion of the second phase inversion as indicated in Fig. 7 (*scale bar* = 50 μm)

Effect of electrolyte. It is well known that the addition of electrolyte to emulsions and dispersions causes destabilisation and subsequently separation as a result of salting out of the surfactant [3, 4, 20]. It is therefore not possible to add high concentrations of electrolyte to the aqueous phase before the first phase inversion. The addition of electrolyte after the first phase inversion also causes separation of the aqueous phase and the polymer melt; however, subsequent mixing and cooling appear to result in the incorporation of the aqueous phase and the formation of electrolyte-solution-in-solid-polymer agglomerates after cooling. The history of this process is shown in Fig. 7. The microcapsules contain 30% salt solution (concentration of NaCl = 25%). After obtaining the electrolyte-solution-in-solid-polymer microcapsules, silica can be added to the system in order to improve the flow characteristic of the powder. The structure of the agglomerates is shown in Fig. 8, which indicates that the large aggregates are formed by the aggregation/fusing of the smaller particles of the polymer.

In Fig. 8a, there is no evidence of NaCl crystals on the agglomerate surface. When these electrolyte-in-solid-polymer microcapsules are added to hydrophilic silica, it appears that the surface of the aggregates are covered by NaCl crystals as shown in Fig. 8b. It is possible that the hydrophilic silica preferentially absorbs water and causes the crystallisation of NaCl.

Conclusions

1. The macromolecular surfactant HMWS-A2 is a useful macromolecular surfactant and can be used to prepare LDPE dispersions. The emulsion droplet size decreases with increasing surfactant concentration up to about 20 wt% of the oil phase.
2. The first phase inversion from a water-in-polymer-melt emulsion to a polymer-melt-in-water emulsion takes place at a critical water-phase volume of 20%.
3. At 20% water content, the emulsion droplets (polymer melt) appear to have a relatively broad distribu-

tion in a close-packed arrangement. When this emulsion is cooled to solidify the polymer melt droplets under static conditions, latex particles are obtained. If, however, the cooling is carried out while mixing, a second phase inversion takes place when the temperature reaches the recrystallisation temperature of the LDPE/macromolecular surfactant binary system. This second phase inversion takes place even if the phase volume of the water is well above 20%. After the second phase inversion, water-in-solid-polymer aggregates are obtained. These aggregates are essentially powders and hence the technique can be used to agglomerate/microcapsule active materials in the presence of water.

4. The flow properties of the water-in-solid-polymer aggregates can be improved by the addition of silica after the second phase inversion.
5. An aqueous phase with large amounts of electrolyte can be encapsulated by the addition of the salt after the first phase inversion; however, if hydrophilic silica is added to this water/electrolyte-in-solid-polymer aggregate, salt within the aggregates appears to diffuse out and form needlelike crystals on the aggregate surface.

Acknowledgements This work was supported by grants from the UK Engineering and Physical Science Research Council, AstraZeneca, Gebruder Haake GmbH and Rosand Precision Ltd. We are grateful for their support.

References

1. Hester CI, Nicholson RL, Cassidy MA (1990) Powder coating technology. Noyes Data Corporation, Park Ridge, NJ, USA
2. Tanaka M, Honma S (1987), European Patent 246 729 A3
3. Akay G (1996) European Patent 649 867
4. Akay G (1998) Chem Eng Sci 53:203–223
5. Akay G, Kazeem A, Chen SY, Choudhery R (1998) In: Recent advances in particle technology CD ROM. Institute of Chemical Engineers, UK
6. Akay G, Tong L (2000) Chem Eng Technol 23:285–289
7. Akay G, Tong L (2000) J Mater Sci 35:3699–3709
8. Akay G, Tong L (2001) J Colloid Interface Sci 239:342–352
9. Akay G (1995) In: Narkis M, Rosenzweig N (eds) Polymer powder technology. Wiley, New York, pp 542–587
10. Akay G (1990) Polym Eng Sci 30:1361–1372
11. (a) Akay G (1991) US Patent, 4,988,369; (b) Akay G (1992) European Patent 382 464; (c) Akay G (1994) Japanese Patent 940 37634
12. Akay G (1993) Australian Patent 633 299
13. Akay G (1994) Polym Eng Sci 34:865–880
14. Akay G, Garrett PR, Yorke JWH (1994) European Patent 593 441
15. Akay G, Chapple A, Garrett PR, Knight PC, Yorke JWH (1994) Australian Patent 651 732
16. Akay G, Downes S, Price VJ (2000) World Patent Publication WO 00/34454
17. Akay G, Irwing GN, Kowalski AJ, D.Machin (1996) World Patent Publication 96/20270
18. Akay G, Wakeman RJ (1997) J Membrane Sci 131:229–236
19. Tant MR, Wilkes GL (1988) J Macromol Sci Rev Macromol Chem Phys C 28:1–63
20. Tadros TF, Vincent B (1983) In: Becher P (ed) Encyclopedia of emulsion technology, vol 1. Dekker, New York, pp 129–285