JOURNAL OF MATERIALS SCIENCE **37** (2002) 4985–4992

Process intensification in particle technology: flow induced phase inversion in the intensive emulsification of epoxy polymer melts in water

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The flow induced phase inversion phenomenon is applied to the phase inversion emulsification of high molecular weight epoxy polymer melt to obtain sub-micron particles. It is found that molecular surfactants could not be used to obtain the initial [water-in-polymer melt] emulsion. Polymeric surfactants, hydrophobically modified water soluble polymers have to be used for this purpose. The molecular structure of the polymeric surfactant is important in obtaining smaller emulsion droplets for a given polymer melt. Depending on the processing history, either a 'powdery dispersion' containing 10 wt% water or water continuous dispersion can be obtained. Sub-micron epoxy particles can be obtained, even at relatively low polymeric surfactant concentrations, by subjecting the [water-in-polymer melt] emulsion to very high deformation rates using a model static mixer called Multiple Expansion Contraction Static Mixer. This mixer is essentially a series of short capillaries separated by flow dividers. In order to provide constant flow rate at very high pressures, an injection moulding machine is used.

1. Introduction

The applications of emulsions include coatings, paints, adhesives, cosmetics, agro-chemicals, pharmaceuticals, food and crude oil [1]. Epoxy based emulsions are extensively used in coating applications (accounting for 80% of the epoxy consumption) [2]. Epoxy resins have recently been emulsified using anionic or cationic surfactants to obtain colloidal emulsions using the Flow Induced Phase Inversion (FIPI) emulsification technique [3–5]. The aqueous phase volume of such emulsions is of the order of 40% so as to obtain sufficiently low emulsion viscosity. Alternatively, it is possible to use high molecular weight epoxy solids in powder form in powder coating applications. Flow induced phase inversion emulsification [3–9] has recently been shown to produce highly concentrated colloidal emulsions using viscous polymeric resins and thermoplastic melts. Such emulsions are very viscous (with a yield stress, i.e., they behave like a Bingham body) and shear thinning thus providing high storage stability and desirable flow characteristics (shear thinning viscosity) in coating applications.

The present authors have recently studied the phase inversion emulsification of molten polymers including highly viscous polymeric resins (such as epoxy resins) [7, 9] and shown the existence of some fundamental difficulties compared with the phase inversion emulsification of oils [3–5]. The most important difference between the emulsification of oils (or polymeric resins) in water is that in polymeric melts, molecular surfactants could not be used, even at high concentrations. Surface activity requirement in emulsification must be provided either by chemical modification (grafting) of the polymer chains or by using macromolecular surface active agents such as hydrophobically modified water soluble polymers (HMWSPs). The molecular structure of HMWSPs is also an important factor in the emulsion formation [6–9]. It was postulated that, due to the surface undulations of the deforming polymeric melt, molecular surfactants are removed from the water-polymer interface and rendered ineffective by being entrapped within the polymer bulk [9].

Another important aspect of polymer melt emulsification in water is that the emulsification temperature can be very high due to the high melting temperature of the polymer, which can necessitate pressurisation. However, standard polymer processing equipment with some modification can be used for high pressure/high temperature emulsification. Furthermore, the lack of any study on the high temperature and pressure behaviour of macromolecular surfactants also restricts the scope of the polymer melt emulsification. It is known that the emulsion stability can decrease with increasing

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pressure as a result of increasing solubility of surfactant in oil or aqueous phases [10].

In our recent studies [6–9], we have evaluated the mechanism of phase inversion emulsification of polymeric melts using polymeric surfactants and shown how the changes from a melt state to solid state (or vice versa) can result in thermo-mechanically driven phase inversions. Such thermo-mechanically driven phase inversions are essentially non-isothermal flow induced phase inversion [FIPI]. The FIPI phenomenon has been applied to process intensification in particle technology [11–16], processing of high internal phase emulsions [17, 18] and the inversion of a water-in-oil, (W/O) emulsion to an oil-in-water, (O/W) emulsion to obtain colloidal emulsions [3, 19]. This phase inversion is achieved without any changes in the thermodynamic state variables (TSVs) but through the application of deformation (flow) which can be characterised by the Deformation State Variables (DSVs), such as deformation rate and vorticity [3, 5].

FIPI is not catastrophic [20] but transient [3–5]. Phase inversion in a given type of flow starts at a critical deformation rate, Σ^*. The type of flow can be qualified by the objective measure of vorticity [5]. The emulsion droplet size decreases, size distribution narrows and the degree of phase inversion increases with increasing deformation rate (Σ) over and above the critical deformation rate. It is therefore important to have a constant deformation rate during phase inversion in order to control the emulsion characteristics. The critical deformation rate is also dependent on the thermodynamic state of the emulsion before it is inverted from a water-in-oil (W/O) to an oil-in-water (O/W) emulsion. A useful measure of the thermodynamic state of the (W/O) emulsion is the phase volume of the aqueous phase, Φ. In the absence of any substantial deformation, (W/O) emulsion can be inverted to an (O/W) emulsion if the aqueous phase volume is increased to a critical value (Φ^*). It was shown [7] that the deformation rate and phase volume fraction deviations from their respective values ($\Delta\Sigma = \Sigma - \Sigma^*$ and $\Delta\Phi = \Phi^* - \Phi$) correlate well for a given emulsion system undergoing phase inversion in a given flow field (i.e., constant vorticity). $\Delta\Sigma$ increases rapidly with increasing $\Delta\Phi$. Therefore, it is possible to obtain highly concentrated emulsions using very high deformation rates and the technique is useful when the critical phase volume Φ^* is high.

We have shown that the critical aqueous phase volume at phase inversion Φ^* is a function of oil phase viscosity and $\Phi^* \rightarrow 0.2$ as oil phase viscosity becomes very large. These experiments have been conducted by using epoxy resins with viscosity ranging from ca. 1 Pa.s to ca. 1000 Pa.s. In the emulsification of the polymeric melts, high viscosity implies that the critical phase volume is constant at ca. 0.2, as indeed confirmed experimentally [7–9].

In order to achieve controlled and uniform deformation rates across the flow field, a model static mixer was used previously [3, 4]. This mixer, called Multiple Expansion Contraction Static Mixer (MECSM) essentially consists of a series of short capillaries, separated by flow dividers. The deformation rate at the capillary entry can be quantified [3, 4, 21–23]. Due to the small processing volume, a very high throughput is necessary to achieve very high deformation rates. Thus this process is inherently intensive. Therefore, the FIPI emulsification technique is deemed to be Process Intensification [24] in particle technology.

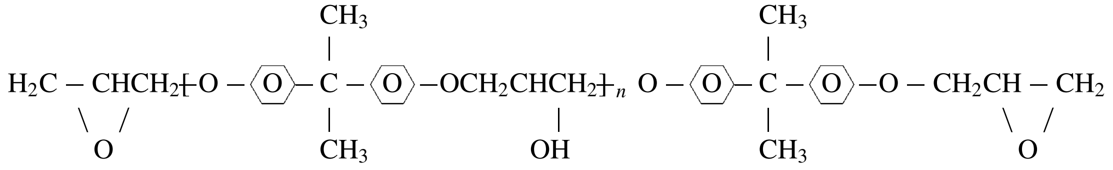
In our previous studies, we have also investigated the mechanism of phase inversion emulsification of thermoplastics such as low density polyethylene [7, 9] and ethylene vinyl acetate copolymer [25]. However, in these studies, we did not investigate the effect of deformation on the size and size distribution of the emulsion droplets. In this study we investigate the effect of flow field on the solid epoxy dispersions prepared by FIPI emulsification.

2. Experimental

2.1. Materials

2.1.1. *Epoxy polymer*

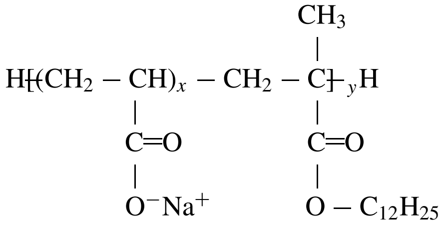
Epoxy resin with the trade name Epikote 1001 was supplied by Shell Chemical Co. Epikote 1001 is solid at room temperature. Its average molecular mass is 950 Da with an epoxide equivalent of 450–525. The epoxide equivalent is the mass of resin in grams which contains 1 gram chemical equivalent of epoxy. The melting range of Epikote 1001 is 64–76°C. The chemical structure is given below [3].



$$\underset{\diagdown\ \diagup\atop O}{H_2C - CHCH_2} \!\left[O - \langle O \rangle - \overset{CH_3}{\underset{CH_3}{C}} - \langle O \rangle - OCH_2\underset{OH}{CH}CH_2 \right]_n O - \langle O \rangle - \overset{CH_3}{\underset{CH_3}{C}} - \langle O \rangle - O - CH_2\underset{\diagdown\ \diagup\atop O}{CH - CH_2}$$

2.1.2. *Hydrophobically modified water soluble polymers (HMWSPs)*

Surface active agents used in this study were coded as HMWSP A-1 and HMWSP A-2. They were experimental HMWSPs supplied by National Starch and Chemical Company (UK). These polymeric surfactants were poly(acrylic acid)/lauryl methacralate sodium salt. The general chemical structure is given below [9]:



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

where $x = 25$, $y = 1.5$ for HMWSP A-1 and $x = 8$, $y = 3$ for HMWSP A-2.

2.2. Equipment

2.2.1. HAAKE Rheometer 9000

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 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 mixer is heated up and the temperature can be controlled using an air cooling system. The torque on the rotors, the change of 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 temperature of the mixer as a function of time.

2.2.2. Multiple expansion contraction static mixer (MECSM)

The Multiple Expansion Contraction Static Mixer (MECSM) is essentially a model mixer described elsewhere [3, 5, 21] for various applications. It was also used to study the rheological characteristics of reinforced polymer melts at high pressures and deformation rates [21–23]. The internal structure of a MECSM is diagrammatically represented in Fig. 1. It consists of several mixing units (we used 4 such units) in series, housed in a stainless steel sleeve. The temperature of the MECSM is controlled by electrical trace heating. Each mixing unit consists of an inlet spacer ring, capillary, outlet spacer ring, followed by a flow divider. The capillary entry and exit angles (ϕ) are 135°. The capillary diameter ($D = 1$ mm) and the capillary length ($L = 2$ mm) were kept constant. The maximum shear rate (Γ_m) and extension rate (Σ_m) in the mixer are calculated from [3, 4, 21]

$$\Gamma_\mathrm{m} = 32Q/\pi D^3 \quad \text{and} \quad \Sigma_\mathrm{m} = 1/2\,\Gamma_\mathrm{m}\sin(\phi/2).$$

where Q is the volumetric flow rate through the capillaries.

2.2.3. Injection moulding machine

An injection moulding machine BA 800/315 CDC (Battenfeld) was used to inject [water-in-epoxy polymer] dispersion 'powdery dispersion' through the mixer. The technique used in this section is essentially similar to that employed in the injection rheometry studies of reinforced polymer melts [21–23]. The use of the injection moulding machine ensures that sufficiently high flow rate through the Multiple Expansion Contraction Static Mixer (MECSM) is achieved and that the flow rate is not affected by the pressure developed during injection. In this system, the mould was replaced by the MECSM unit which was connected to a small jacketed batch mixer as shown in Fig. 2. The MECSM was kept at 80°C. The temperature (80°C) is slightly above the melting point of the epoxy polymer so that the mixture forms into a viscous melt. The batch mixer was kept at 25°C and it contained dilution water. The batch mixer was fitted with an impeller the speed of which was kept at 300 rpm. The material injected by the injection moulding machine passed through the MECSM and entered into the batch mixer where it was diluted immediately and cooled subsequently to obtain solid epoxy dispersion. In order to operate the injection moulding machine under these conditions, a new operating programme was installed in the servo-control of the machine.

Temperatures of all zones along the barrel, nozzle and MECSM were the same, at 80 ± 5°C, for the same reason as above, so that the maximum achievable viscosity conditions were maintained. The maximum pressure available in the injection unit was 140 bar which creates maximum shear rate of $4.0 \times 10^5\ \mathrm{s^{-1}}$, and the corresponding extension rate of $1.85 \times 10^5\ \mathrm{s^{-1}}$. After the injection, the pressure at the nozzle decayed and the experiment was terminated. This system allows the processing of small quantities of emulsions at very high deformation rates.

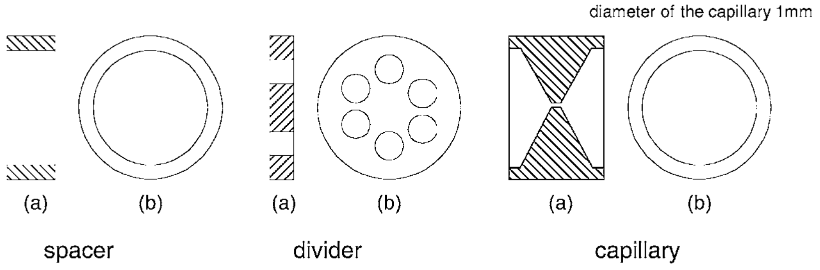


Figure 1 Elements (spacer, divider and capillary) of a single unit of the Multiple Expansion Contraction Static Mixer (MECSM) model mixer where the shear and extensional deformation rates can be quantified. (a) Cross-sectional view. (b) Plane view of the mixer elements.

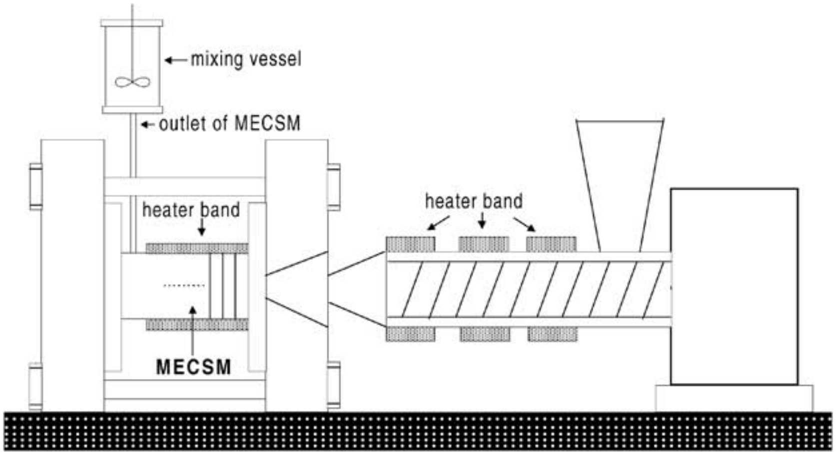


Figure 2 Injection moulding machine combined with MECSM.

2.2.4. Scanning electron microscopy (SEM)

The morphology of the emulsions was examined by SEM which was performed using a Hitachi S-2400 Scanning Electron Microscope. Emulsion samples were prepared for SEM by drying a drop of emulsion on a specimen mount. Powdery emulsion samples were fractured in liquid nitrogen or at room temperature then stuck onto stubs using double sided conductive adhesive tape. All the samples were gold coated.

2.2.5. Particle size and size distribution analysis

The particle size and size distribution analyses were performed using a Malvern Mastersizer which is based on the laser diffraction technique. 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, 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 particle diameters below which 90, 50 and 10% of the particles lie respectively. The particle size distribution as well as various particle sizes were computed by using the software available in the Malvern Mastersizer.

2.3. Epoxy emulsion preparation

In a typical emulsion preparation, Epikote 1001 and sufficient amount of HMWSP solution were mixed in the HAAKE mixer to obtain 90% Epikote and 10% HMWSP on dry basis. The mixer was kept at constant temperature, 70°C. The mixer had a reflux condenser to collect the water evaporated from the mixture. This allowed determination of the amount of water present in the emulsion which was also checked independently by drying the dispersion and recording its water content. During mixing, torque was recorded as shown in Fig. 3. As water was removed from the mixture, the mixer torque increased and at about 10% water level, a powdery emulsion was obtained. In this case, the emulsion did not go through a phase inversion stage. Small amounts of samples were recovered from the mixer at various stages for SEM examination. When the mixer torque reached a plateau (water content is ca. 1%), water was dosed into the mixer at a rate of 1.5 g/min through the reflux condenser which returned any evaporated water back into the mixer. When the torque dropped very sharply, [water-in-polymer melt] was phase inverted to a [polymer melt-in-water] emulsion as indicated in Fig. 3. After the formation of the [polymer melt-in-water] emulsion, water addition was continued to dilute the emulsion (to 35% water) and subsequently, emulsion was allowed to cool without any further mixing in order to prevent any phase re-inversion as observed in our previous studies [7–9].

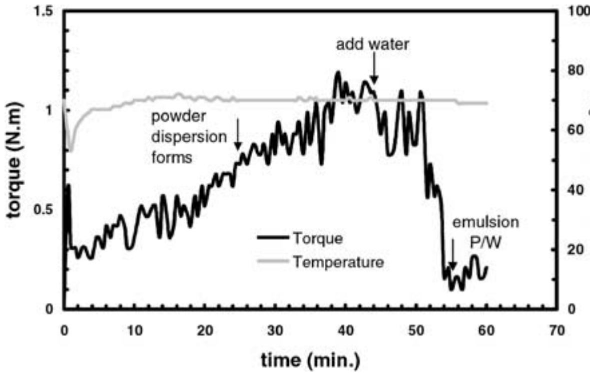


Figure 3 The emulsification history of the epoxy polymer (90% Epikote 1001 and 10% HMWSP A1) at 70°C. Samples are taken when the 'powdery dispersion' and the final (epoxy polymer melt-in-water) emulsion are obtained. Final emulsion was further diluted and cooled to obtain 35% water. P/W = (Polymer melt-in-Water) emulsion.

When the MECSM was used to achieve phase inversion at very high deformation rates, [water-in-solid polymer] dispersion was prepared which contained 10% water. This was achieved by mixing 90% polymer and 10% HMWSP A1 (on dry basis) and subsequently water was evaporated completely. In this case, the mixer torque reached 1.1 Nm. Water was dosed in (1.5 g/min) to obtain [water-in-polymer melt] emulsion containing 10% water. This dispersion was then fed into the injection moulding machine and injected through the MECSM.

3. Results and discussion

3.1. Effect of stress on particles size

During the mixing of the surface active material (in water) with the polymer melt (see Fig. 3), the formation of polymer droplets could already be observed even before phase inversion [7, 9]. The sample taken from the high torque Haake mixer when the torque was 0.7 Nm had 10% water and it could be dispersed in water to obtain a dispersion for particle size measurement. This type of dispersion was termed as 'powdery dispersion' by Tanaka and Honma [26] who used a mixture of several surfactants and electrolytes to obtain such polymer dispersions at low water content. Since this dispersion could be dispersed in water, it was assumed that the powdery dispersion was water continuous. The appearance of this powdery dispersion is shown in Fig. 4 where no additional water was added to dilute the dispersion. In order to have dispersed phase particles above 72%, the particles should be deformable to create close-packed polyhedral structures (as in high internal phase emulsions) or the particle size distribution should be specific (multi-modal) [27]. As seen from Fig. 4, the particles of the 'powdery dispersion' do not have polyhedral structure and although there is some evidence of multi-modal particle size distribution, there is no evidence of close packing. We therefore conclude that the powdery dispersion is not water continuous but the particles are weakly bound and are easily dispersed in water. Nevertheless, this material is useful for powder coating as the primary particle size is relatively small ($\cong 3$ μm) as shown in Fig. 4.

When water was added to this dispersion, and mixed further after obtaining the powdery dispersion, the appearance of the material was more discrete as shown in Fig. 5. If the mixing was continued to reach a torque plateau at 1.1 Nm and subsequently water was added to obtain a [polymer melt-in-water] emulsion, the resulting particle size was significantly smaller compared with the emulsion produced at 0.7 Nm as shown in Fig. 6. It is also interesting to note that the particles appear to be distorted and have a close packed structure. This is a result of the reduction of the water phase at high torque as a result of further water evaporation. Even though the dispersion was diluted by water addition, the shape recovery to spherical form did not materialise. The particle size characteristics are summarised in Table I. These results indicate that the present polymer/HMWSP system also displays the characteristics of the previously investigated polymeric systems [9] as regards the effect of stress on particle size.

TABLE I The effect of stress on emulsion particle size characteristics when [90% Epikote 1001 and 10% HMWSP A1] was emulsified at two different stress levels as quantified by the torque on the mixer blades

Maximum torque	Span	D (μm) $D[4, 3]$	$D[3, 2]$	$D[v, 0.9]$	$D[v, 0.1]$	$D[v, 0.5]$
0.7 Nm	2.05	3.77	1.16	7.42	0.41	3.42
1.2 Nm	1.61	3.06	0.79	4.52	0.36	2.60

3.2. Effects of chemical structure and concentration of surface active material

In our previous studies, we observed that the emulsion particle size, under identical processing conditions is affected by the chemical structure of the HMWSP [9, 25]. HMWSPs A1 and A2 have similar molecular weights (4 kDa and 3 kDa respectively) and the hydrocarbon chain length of the hydrophobic anchorage (tail) groups in both surfactants are identical ($C_{12}H_{25}$). However, the average number of anchorage groups in A1 and A2 are 1.5 and 3 per molecule, while the numbers of hydrophilic groups per hydrophobic tail group are 25 and 8 respectively. Table II shows that HMWSP A1 is a more effective surface active agent than HMWSP A2 as far as

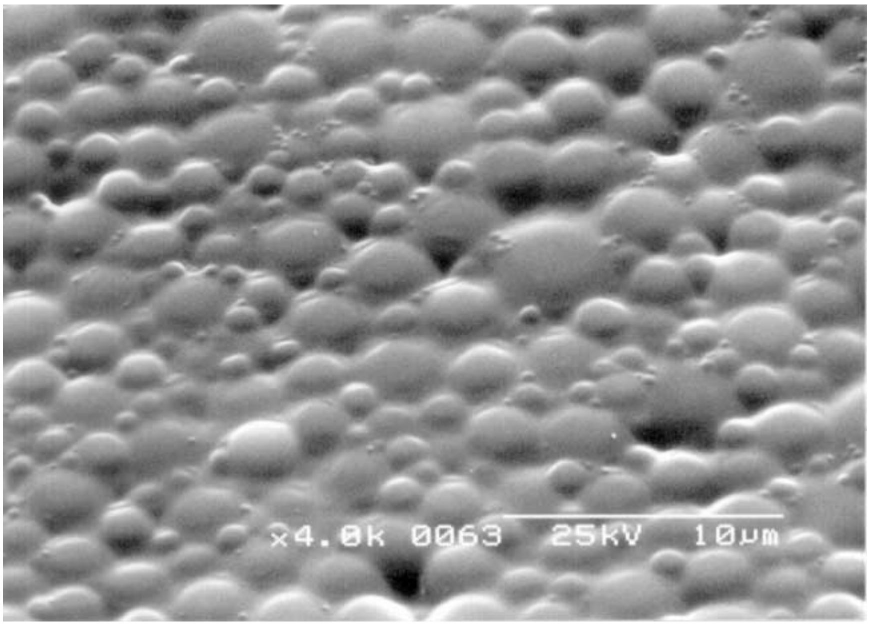


Figure 4 SEM micrograph of epoxy powdery dispersion sample containing 90% Epikote 1001 and 10% HMWSP A1. Sample was taken when the mixer torque was 0.70 Nm. The sample was fractured in liquid N_2, and then gold coated. Scale bar = 10 μm.

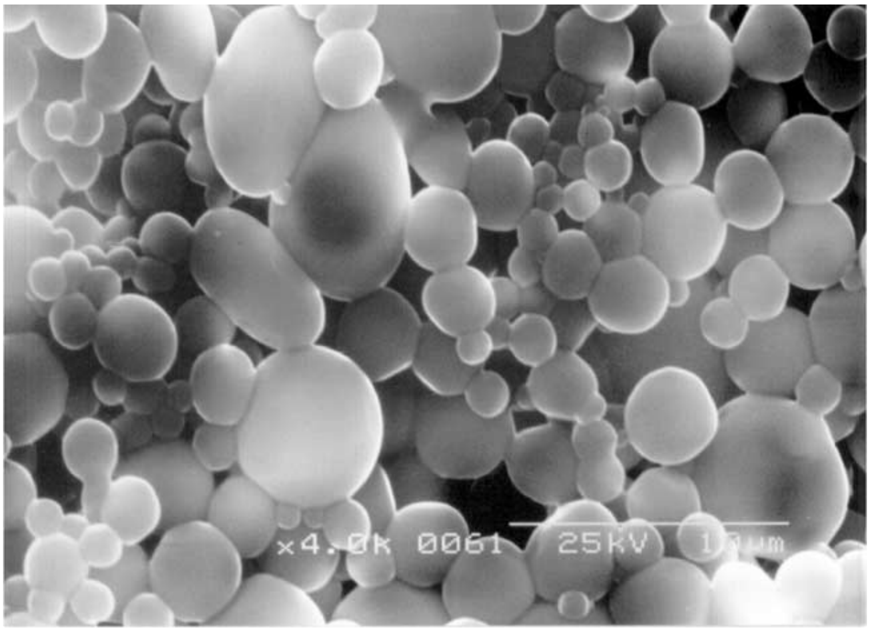


Figure 5 SEM micrograph of epoxy powdery dispersion sample after it was dispersed in water. The sample was removed at the same time as the sample in figure 4 followed by dispersion in water. A drop of this dispersion was dried on a specimen stub and gold coated after drying. Scale bar = 10 μm.

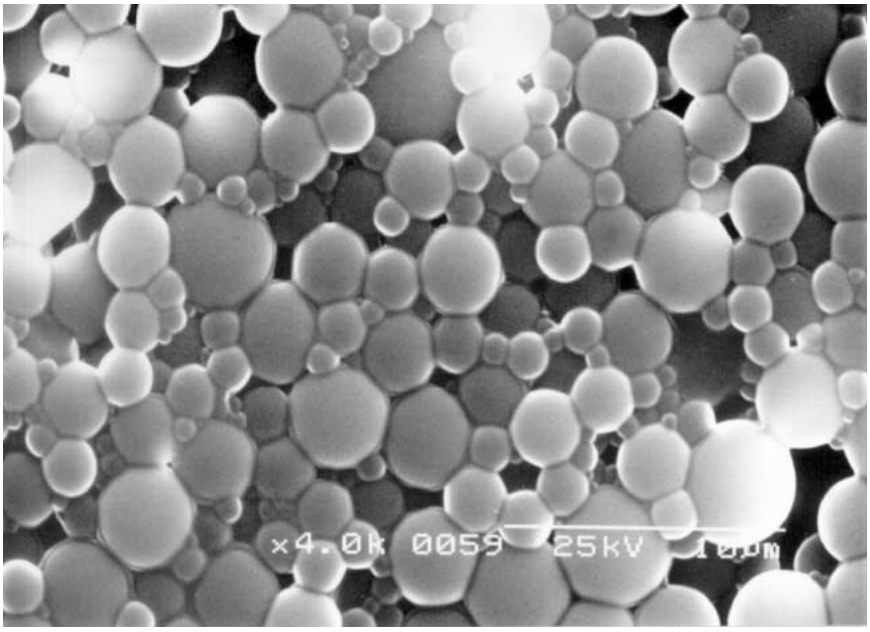


Figure 6 SEM micrograph of epoxy powdery dispersion prepared from 90% Epikote 1001 and 10% HMWSP A1 which are mixed together until the torque reached 1.2 Nm and water was dosed to obtain a [Water-in-Polymer melt emulsion] which was subsequently phase inverted to obtain [Polymer melt-in-Water] emulsion when water content reached 20%. Water addition was continued until the water content was 35%, Scale bar = 10 μm.

the emulsion droplet size is concerned. In our previous studies, it was found that for low density polyethylene (LDPE) [7, 9] and ethylene vinyl acetate copolymer (EVA) [25], the preferred surfactants (to obtain smaller dispersion size) were A2 and A1 respectively. Based on our previous conclusion if the molecular weight of the polymer is high, the number of anchorage tail groups of the surfactant should be large in order to ensure that

TABLE II Particle size analysis of Epikote 1001 emulsion using two different HMWSPs and concentrations when the emulsification was carried out at the maximum mixer torque of 1.2 Nm

			D (μm)				
HMWS P type	HMWPS wt% in epoxy	Span	$D[4, 3]$	$D[3, 2]$	$D[v, 0.9]$	$D[v, 0.1]$	$D[v, 0.5]$
A1	10	1.61	3.06	0.79	4.52	0.36	2.60
	20	3.93	1.06	0.39	2.02	0.21	0.46
A2	20	2.40	1.58	0.61	2.09	0.32	0.74

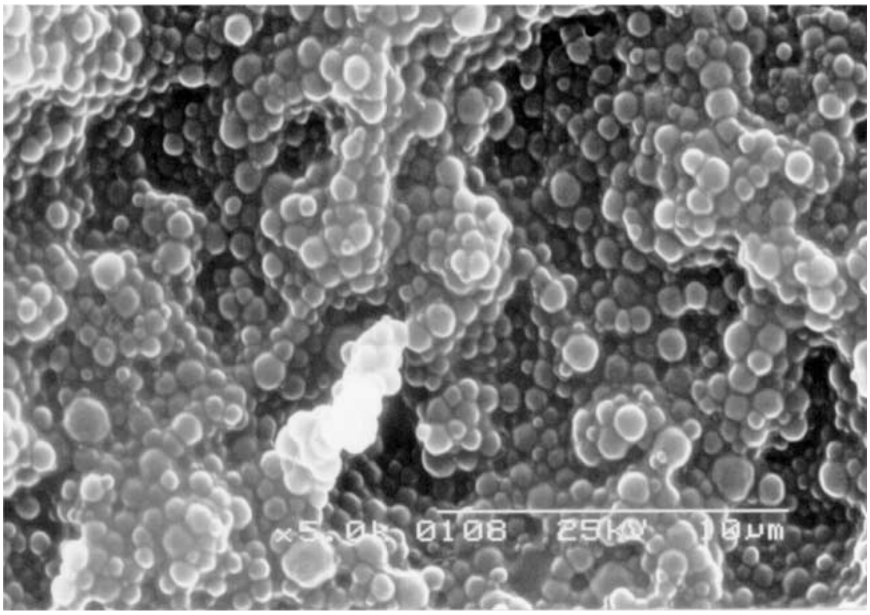


Figure 7 SEM micrograph of the epoxy powdery dispersion after injection through the MECSM (maximum shear rate was 4.0×10^5 s^{-1}). The dispersion contained 90% Epikote 1001 and 10% HMWSP A1. Water content of the powdery dispersion was 10% before the SEM examination. Sample was fractured in liquid nitrogen and then gold coated. Scale bar = 10 μm.

the surfactant remained at the water/polymer melt interface. However, examination of the chemical structure of LDPE, EVA, epoxy polymer (Epikote 1001) and the surfactants, A1 and A2 indicates that the better performance by the surface active HMWSP may also depend on the hydrophobicity (i.e., hydrophile-lipophile balance, HLB) of the polymer and surfactant.

Since LDPE is more hydrophobic than EVA or epoxy polymer, the use of a more hydrophilic surfactant (HMWSP A2) with LDPE will ensure that the surface active material would remain at the water/polymer melt interface rather than be removed from the interface into the bulk of the polymer melt as described previously [9]. A similar argument also applies to the HMWSP A1/EVA or Epoxy polymer systems. We note that HMWSPs A1 and A2 do not dissolve in water but they can be dispersed as aggregates in water. Coupled with our previous results [3–9], the current results indicate that the effect of the chemical structures of the surfactant and polymer on the emulsion droplet size needs to be investigated further. When molecular surfactants are used with polymeric resins [3], the efficiency of emulsification is dependent on the chemical structure of the surfactant even when surfactants with very similar hydrophile-lipophile ratio (HLB = 8.3 ± 0.3) are used. In fact, we also used the same molecular surfactants employed in the emulsification of the epoxy resins [3] in this present study but we were unable to obtain any [water-in-polymer melt] emulsion in the first instance to phase invert to obtain the [polymer-in-water] dispersion. The processing conditions used in these failed experiments were the same as those when HMWSPs were used as surfactants with EVA.

The effect of surfactant concentration on the particle size is also illustrated in Table II. As seen here, the use of 10% surfactant (and 90% polymer) results in relatively large dispersion size compared with the case when 20% surfactant is used. It is also interesting that, with LDPE the minimum amount of surfactant (A2) needed to achieve emulsification was 15% [9]. Reduced surfactant use in emulsions is highly desirable in most applications.

TABLE III The effect of shear rate on particle size characteristics of 90 Epikote 1001 and 10% HMWSP A1

Sampling time	Span	D (μm)				
		$D[4, 3]$	$D[3, 2]$	$D[v, 0.9]$	$D[v, 0.1]$	$D[v, 0.5]$
Before injection	1.61	3.06	0.79	4.52	0.36	2.60
After injection	1.50	0.74	0.68	0.81	0.18	0.42

3.3. Effect of shear rate on particle size

The phase-inversion emulsification experiments carried out using the high torque Haake mixer in batch mode represent essentially an investigation of the effect of thermodynamic state variables on emulsification of polymer melts. In order to investigate the effect of deformation state variables on phase inversion and emulsion characteristics, we use the Multiple Expansion Contraction Static Mixer (MECSM) in conjunction with an injection moulding machine. The results of these experiments are summarised in Table III. In these experiments, polymer melt contains 10% HMWSP A1 and the aqueous phase content of the starting [water-in-polymer melt] emulsion is 10%. When the emulsion emerged from the MECSM, it was immediately diluted in the batch mixer and subsequently cooled. As seen from Table III, the polymer particle size is reduced considerably compared with that in the emulsion obtained at low deformation rates using the high torque Haake mixer. The appearance of the dispersion immediately after it emerged from the MECSM is shown in Fig. 7

which indicates a similar structure to the 'powdery dispersion' but the particles are more discrete and smaller. It is therefore possible to obtain colloidal polymeric dispersions at low surfactant concentrations but at very high deformation rates.

The injection moulding machine provides the necessary power and precision required to pump a small amount of emulsion at very high flow rates through the MECSM at constant pressure. In industrial applications, the injection moulder would be replaced by an extruder operating at high flow rates and pressures in a continuous process.

4. Conclusions

The Flow Induced Phase Inversion phenomenon was applied to the emulsification of high molecular weight epoxy polymer in the melt state to obtain sub-micron particles. In line with our previous studies, it was observed that molecular surfactants could not be used in the emulsification process at the [water-in-polymer melt] stage. Therefore, two types of polymeric surfactants (hydrophobically modified water soluble polymers) were used as the surface active material. These polymeric surfactants have identical molecular structure but differ by the number of tail groups (anchors) per molecule and the hydrophobicity of the polymer backbone. If the polymer to be emulsified is highly hydrophobic (e.g., low density polyethylene, [7–9]) then more hydrophilic polymeric surfactant (i.e., HMWSP A-2) yields smaller droplets at the same surfactant concentration. In the case of less hydrophobic polymers (e.g., ethylene vinyl acetate co-polymer, EVA [25], and epoxy polymer used in the current experiments), more hydrophobic polymeric surfactant, HMWSP A-1, yields smaller droplets. We also note that the number of anchor groups per surfactant molecule is twice as much in A-2 compared with the surfactant A-1. Therefore, the present observations do not exclude the conclusion [9] that the higher the molecular weight of the polymer, the higher the number of anchor groups in the polymeric surfactants in order to ensure that the surfactant remains at the polymer melt/water interface.

It is possible to obtain a 'powdery dispersion' in which the water content of the dispersion is ca. 10%. This emulsion can be dispersed in water to give a concentrated emulsion if desired. Such emulsions are useful in powder coating. The size and the spread of the size distribution (span) of the emulsion droplets after phase inversion from a [water-in-polymer melt] emulsion to a [polymer melt-in-water] emulsion decreases with increasing stress during mixing of the polymer melt and water. However, if the phase inversion is carried out at very high deformation rates, emulsions with very small size span and sub-micron size particles can be obtained. Emulsification at the maximum shear rate of $4.0 \times 10^5\ \mathrm{s}^{-1}$ was carried out using a Multiple Expansion Contraction Static Mixer (MECSM) attached to an injection moulding machine which provided constant flow rate at very high pressures [21–23]. The use of this type of equipment is necessary in order to process small quantities of polymer at very high flow rates under very well controlled conditions. However, emulsification of polymer melts at very high deformation rates in industrial scale can be achieved using twin screw extruders in conjunction with a MECSM or a dynamic version of MECSM [3, 19].

Acknowledgements

This work was supported by grants from the UK Engineering and Physical Sciences Research Council (EPSRC), Carl Stuart Ltd., ICI Strategic Research Funds, ICI Paints, National Starch and Chemical Co., Thermo Haake and Unilever Research. We are grateful for their support. We thank Drs. R. A. Choudhery and K. Murray (ICI Paints) and Dr J. Watkins (National Starch and Chemical Co.) for the measurement of the particle size of the dispersions, for the supply of the experimental surface active materials, and for many helpful discussions.

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Received 23 April 2001
and accepted 12 June 2002