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Preparation of ethylene vinyl acetate copolymer latex by flow induced phase inversion emulsification

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Ethylene vinyl acetate (EVA) copolymer was emulsified in the melt state using hydrophobically modified water soluble polymers (HMWSPs) as surfactants and the flow induced phase inversion (FIPI) emulsification technique. The history of the emulsification and emulsion structure were monitored using a process rheometer and off-line scanning electron microscopy and particle size measurements. It was shown that low molecular weight surfactants could not be used to emulsify the polymer melt. When HMWSPs were used, the emulsion characteristics were strongly influenced by the molecular structure of the surfactant. Water-in-polymer melt emulsion was phase inverted to polymer melt-in-water emulsion at 20% water phase volume. When this emulsion was allowed to cool after further dilution (30% water) while mixing, a second phase inversion took place to obtain a water-in-polymer dispersion which has the consistency of a powder. When this dispersion was re-heated, while mixing, a third phase inversion occurred and a multiple emulsion system was obtained. Upon the solidification of the polymer, the structure of the dispersion was revealed as (water-in-polymer)-in-water. Water continuous latex from the first phase inversion and the powdery emulsion from the second phase inversion can be used in coating applications while the third phase inversion produces micro-porous polymer. © *2002 Kluwer Academic Publishers*

1. Introduction

Powder coating is an environmentally friendly finishing process since production of these coating systems is solvent-free. Also powder coatings have good performances, for instance, good adhesion, high gloss, light and heat stability, good resistance to scratching, staining, alkaline environment and humidity. Therefore, it is rapidly expanding to more markets and wider applications (i.e., coating on glass bottles, pipes, steel containers, cans, drums). Conventional powder coating technology involves the formulation of a coating from solid components, melt mixing, dispersing pigments (and other insoluble components) in a matrix of the major binder components, and pulverization of the formulation. The powder is applied to the substrate, usually metal, and fused to a continuous film by baking. Thermosetting and thermoplastics powders are available; the major portion of the market (>90%) is for thermosetting type [1].

Polymer latexes form the bases of many paints, adhesives and textile coatings. The latexes made by the procedures described below have been developed for powder coating applications. Currently, latexes are manufactured exclusively by emulsion polymerization which, although well established, is restricted to certain types of monomers and polymerization chemistry [2, 3]. The polymerization rate is in general slower compared with bulk polymerization at high monomer concentrations. Although there are studies to intensify emulsion polymerization through continuous processing [3], the chemical kinetics of the process limit the scope of the improvements in the reaction rates. Furthermore, the residual monomers from the latexes and process water have to be removed and hence the process is essentially environmentally hostile. On the other hand, the waterborne polymer latexes are environmentally friendly coating products.

Flow induced phase inversion (FIPI) emulsification [4–6] has recently been shown to produce highly concentrated colloidal emulsions using viscous polymeric resins. Such emulsions are very viscous (with yield stress, i.e., they behave like a Bingham body) and shear thinning thus providing high storage stability and desirable flow characteristics in coating applications. It is found [4–6] that emulsion viscosity is primarily dictated by the concentration of the ionic surfactant

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and that of the dispersed phase volume. Ionic surfactant must be in the lamellar dispersion phase in the emulsion. It is also shown [4–6] that phase inversion from a water-in-oil (W/O)—emulsion to an oil-in-water (O/W)—emulsion can be achieved by subjecting the W/O emulsion to very high deformation rate flows using mixers with a small volume. Therefore such FIPI based processes are inherently intensive and represent Process Intensification in micro-structured fluids, also known as Intensive Structuring [7].

The FIPI emulsification technique was also applied to the phase inversion emulsification of polymeric melts to obtain colloidal latexes for coating applications. In our previous studies [8–10] on the phase inversion emulsification of thermoplastics, we have shown that colloidal low density polyethylene (LDPE) latexes could be obtained using hydrophobically modified water soluble polymers (HMWSPs) as surface active agents. It has been shown that the molecular surfactants could not be used in the emulsification of LDPE polymer melt in water [8, 9]. However, HMWSPs could be used successfully in the emulsification of LDPE melts provided that the molecular structure of these surface active polymers conform to certain restrictions [9].

Phase inversion emulsification is a well-known technique to obtain colloidal emulsion with a narrow particle size distribution [11, 12]. Inversion from the initial emulsion of [water-in-oil] to the ultimate [oil-in-water] emulsion can be achieved through the changes in the thermodynamic state variables [TSVs] of the oil/aqueous phase/surfactant system such as phase volume, temperature, surfactant concentration and type, viscosity ratio of the phases. However, the kinetics of the phase inversion and microstructure of the final emulsion is dependent on the type of change in the TSVs. When the phase inversion is achieved through the phase volume change, the phase inversion is catastrophic [13, 14]. The phase inversion is transitional if the surfactant's affinity for oil and water is changed through the changes in temperature which affects the hydrophile–lipophile balance (HLB) [13, 14]. During transitional inversion, multiple emulsion of the form {[oil-in-water]-in-oil} or {[water-in-oil]-in-water} may form. Alternatively, phase inversion can be achieved by subjecting the [water-in-oil] emulsion to well defined deformation (flow) to obtain, ultimately, an [oil-in-water] emulsion. This type of emulsification is known as flow induced phase inversion-emulsification [4–6]. The flow induced phase inversion (FIPI) phenomenon is encountered in multi-phase fluid systems as a result of fluid micro-structure/flow-field interactions [4, 5, 15–18]. The macroscopic manifestations of such microscopic interactions are very important in many fields of science, engineering and medicine (see for example [15]). In FIPI-based processes such as agglomeration and micro-encapsulation of powders [5, 16, 17, 19], intensive processing of lytropic liquid crystal dispersions [7] and process intensification in emulsion technology [4, 6], the detailed mechanism of phase inversion can be different. It is dependent on the type of multi-phase (dispersion) system.

FIPI-emulsification exhibits the characteristics of both "catastrophic" and "transitional" phase inversion emulsification. It is therefore possible to obtain stable multiple emulsions (such as {[water-in-oil]-in-water}through this method. Such emulsions are important in drug delivery systems [12] and can also be obtained through the dispersion of [water-in-oil]-emulsions in water. In the FIPI emulsification of highly viscous oils, such emulsions have also been observed. Such multiple dispersions are a common feature of processes giving agglomerates/micro-capsules when fine particles are agglomerated/micro-encapsulated through a phase inversion of [particle-in-polymer melt] to [(particle-in-polymer melt)-in-powder] in which the polymer melt is subsequently solidified to form free-flowing powder as products [8–10].

Phase inversion as a result of phase change (i.e., solidification) is well known in the phase inversion emulsification of [water-in-fat/oil] type of systems (i.e., margarine and low fat spreads) in food emulsions [20]. In the processing of these food emulsions, initially an [oil-in-water] emulsion is obtained above the melting temperature of the fat and this emulsion is subsequently phase inverted by cooling the emulsion while mixing. Here, too, flow (mixing) plays an important role of providing collisions between the emulsion oil droplets which also undergo a phase change during cooling [20].

We have already shown that the molecular surfactants cannot be used to emulsify polymer melts in water. Instead, macromolecular surfactants in the form of HMWSP, are used successfully for the emulsification of low density polyethylene (LDPE) melt which subsequently undergoes solidification to form colloidal particles. The incorporation of colloidal silica is shown to improve the film forming characteristics of the dispersions [8]. In this current study we emulsify ethylene vinyl acetate copolymer in water and investigate the effect of molecular structure of the polymeric surface active materials on the emulsification and emulsion characterisation. We also investigate the mechanism of phase inversions observed during processing.

2. Experimental

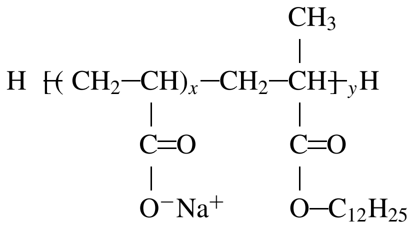
2.1. Materials

2.1.1. Ethylene vinyl acetate

Ethylene vinyl acetate (EVA) was used in the current study and supplied by Etochem which was coded as EVA 28-150 with $M_n = 19000$, density of 1190 kg/m^3 and softening point of 67°C.

2.1.2. Hydrophobically modified water soluble polymers (HMWSPs)

Hydrophobically modified water soluble polymers (HMWSPs) are used as surface active agents. Two grades of these poly(acrylic acid)/ lauryl methacrylate sodium salt were prepared. They were coded as HMWSP-A1 and HMWSP-A2. The general chemical structure of these HMWSPs is given below:



$$H\{(CH_2-CH(C{=}O)(O^-Na^+))_x-CH_2-C(CH_3)(C{=}O)(O-C_{12}H_{25})\}_yH$$

where $x = 25$, $y = 1.5$ for HMWSP-A1, and $x = 8$ and $y = 3$ for HMWSP-A2.

2.1.3. Molecular surfactants

The nonionic surfactants used are commercially available ethoxylated alcohols and esters chosen in such a way that the mean hydrophile–lipophile balance (HLB) is 8.3 ± 0.3. They are Neodol 91-2.5 (primary alcohol ethoxylate, HLB = 8.1; from Shell Chemicals); Cithrol 4DO poly(ethylene glycol) (MW = 400) dioleate, HLB = 8.5; Cithrol 4DL poly(ethylene glycol) (MW = 400) dilaurate, HLB = 8.6; Cithrol 2MO poly(ethylene glycol) (MW = 200) monooleate, HLB = 8.0, and Span 20 (sorbitan monolaurate, HLB = 8.6; from ICI). Cithrol series were provided by Croda Chemicals. The anionic surfactant, sodium dioctyl sulfosuccinate, is supplied by Cyanamid under the trade name Aerosol OT (AOT).

2.2. Equipment

2.2.1. HAAKE high torque mixer: Rheocord 9000

The equipment employed to prepare the EVA emulsions was a high torque rheometer (HAAKE Rheocord 9000) fitted with a mixer Rheomix 3000. The detail of the rheometer can be found elsewhere [8–10]. The torque and temperature are recorded as functions of time. The torque and temperature data can be used to evaluate the phase inversion during the emulsification process. The mixer was fitted with a reflux condenser when needed to prevent water loss through evaporation.

2.2.2. Scanning electron microscope (SEM)

SEM studies were performed using a Hitachi-S-2400 scanning electron microscope. Specimens for SEM study were sampled at different processing stages. Emulsion samples for SEM were prepared by drying a drop of emulsion on a specimen mount. After drying, the samples were carbon-coated and examined under SEM.

2.2.3. Particle size and size distribution analysis

EVA latexes particle size and size distribution analyses were performed using a Malvern 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 characterized 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.

2.3. Emulsion preparation

The experimental procedure is as follows. EVA(140 g) granules and appropriate amount of HMWSP solution (containing 33% HMWSP-A1, or 25 wt% HMWSP-A2) were mixed together in a beaker, so as to obtain 20% HMWSP and 80% EVA on dry basis. The HAAKE Rheocord mixer was programmed to heat up to 120°C. When the temperature of the mixer was 45°C the EVA/HMWSP mixture was placed in the mixer and the rotor was turned on (60 rpm). The torque value 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 water loss through 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 mixer at a rate approximately 1.5 g per minute. The addition of water resulted in a steady drop in the mixer torque, indicating the presence of some free/unincorporated water. The temperature of the mixer was kept at 105°C well above the EVA melting temperature of 67°C. When the water concentration reached a certain value, EVA melt-in-water emulsion was formed [8, 9].

3. Results and discussions

3.1. Mixing behaviour of EVA and HMWSP

The mixing behaviour EVA resin and its blends with HMWSPs is shown in Fig. 1. The mixer was heated up from room temperature to 120°C and kept at this temperature during mixing. The mixing speed was 60 rpm, no water was added during the experiment. When mixing EVA with HMWSP dispersions, no reflux condenser was used, allowing evaporation of all the water. The mixing curves illustrate the rheological behaviour of the polymer and blends. The mixing curves indicate that the EVA + HMWSPs do not have a large torque peak due to the presence of water which is continuously evaporated during mixing. The steady state torque of EVA and EVA + HMWSP A1 blend has very similar values while EVA + HMWSP A2 blend has substantively lower torque.

3.2. Flow induced structure development

Fig. 2 illustrates a typical emulsification history in which the mixer torque and temperature are shown as a function of time. When the mixing of EVA and HMWSP dispersion was started at the mixer temperature of 120°C, the torque started increasing as water

TABLE I Particle size and stability characteristics of EVA emulsions produced by using two types of surfactants, HMWSPs A1 and A2

			Particle size characteristics ($D\mu$m)				
Latex	Stand time month	Span	D[4, 3]	D[3, 2]	$D[v, 0.9]$	$D[v, 0.1]$	$D[v, 0.5]$
EVA-A1 (20%)	0	3.27	3.55	1.21	5.60	0.62	1.52
	14	2.69	3.98	1.32	6.21	0.62	2.08
EVA-A2 (20%)	0	2.65	31.09	3.97	71.26	1.40	26.41
	14	2.36	29.39	4.78	63.45	2.45	25.89

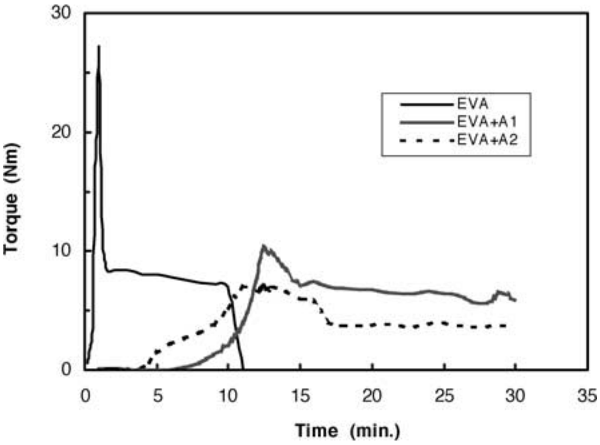


Figure 1 The variation of torque with time during the mixing of EVA or 80% EVA + 20% HMWSPs (A1 or A2). For the neat EVA sample, the mixer was heated up from room temperature to 120°C, and then kept at constant temperature. Rotor speed was 60 rpm. The material was added at $t = 0$. The immediate effect was for the viscosity to increase to a maximum as the EVA granules melted, then a reduction in viscosity was observed as the material continued to heat up. For EVA + A1 and EVA + A2 samples, the mixer was heated up to 120°C; during the heating programme, when the temperature reached to 60°C, the materials were added. The torque values for these samples were increasing steadily due to water evaporation. After water was completely lost from the system then the torque reached the maximum and then dropped down to a steady level. The temperature was kept at 120°C, and the rotor speed was 60 rpm.

evaporated. The torque reached a maximum value of ca. 16 Nm, indicating that all water was evaporated. At this stage, the mixer was fitted with a reflux condenser and water was titrated at a rate of 1.5 g/min. The mixing of EVA and HMWSP before the start of water titration was not prolonged since it was shown that prolonged mixing resulted in the loss of HMWSP from the interface [9]. This resulted in larger emulsion droplets.

As the addition of water to the EVA + HMWSP mixture continued, the torque dropped rapidly due to the presence of unincorporated water. During this stage, the temperature was also reduced to ca. 105°C. Note that due to the electrolytic nature of HMWSP, the boiling point of water was approximately 110°C. When the amount of water reached 20%, phase inversion from [water-in-polymer melt] to a [polymer melt-in-water] took place which was accompanied by a sharp drop in torque as indicated in Fig. 2. After taking a small amount of sample, water addition and mixing at 99°C were continued to dilute the emulsion to 30% water. Once again, a small amount of sample was obtained. These samples were used to confirm the water content of the emulsion, and to determine particle size and observe particle morphology by SEM.

Emulsion dilution from 20% water to 30% water was conducted at 99°C while mixing at 60 rpm for 30 minutes. Fig. 3 illustrates the morphology of the emulsion droplets, while the particle size characteristics are shown in Table I.

Following the first phase inversion and 30 minutes of mixing, the mixer temperature was lowered to 45°C. Cooling and solidification can be conducted while mixing. However, if the solidification was conducted while mixing, a phase re-inversion, i.e., the second phase inversion occurred thus forming a multiple dispersion of the type [(polymer-in-water)-in-polymer]. The second phase inversion can be identified in Fig. 2. The second phase inversion is not sudden but gradual. After the completion of the second phase inversion to obtain a [water-in-solid polymer] a sample was taken and examined under SEM. Fig. 4 illustrates the appearance of the dispersion which was diluted to obtain 30% water and cooled from 99°C to 50°C while mixing. As seen in Fig. 4, this dispersion is still in a particulate form but compared with the dispersion before cooling while mixing (i.e., Fig. 3), it has signs of phase re-inversion and size enlargement with several dimpled particles. After the completion of the second phase inversion, a co-continuous system was obtained as illustrated in Fig. 5. It can be seen from Fig. 5 there is extensive particle/particle aggregation resulting in a porous structure. The particles forming aggregates also appear to contain dimples, similar to these observed in Fig. 4. A third phase inversion took place when the [water-in-solid polymer] was re-heated from 45°C while mixing. The third phase inversion started at 48°C (as deduced from the reduction in torque as seen in Fig. 2). The heating/mixing were continued until the melt temperature reached to 90°C. When the temperature dropped down to 80°C, another sample was taken. The appearance of this water continuous dispersion is shown in Fig. 6.

3.3. Particle size characteristics and emulsion stability

The particle size measurements of various emulsions are summarised in Table I. In all cases, the emulsion was obtained after the first phase inversion and subsequently diluted while mixing at 99°C for 30 minutes to obtain a [polymer-in-water] emulsion containing 30% water. Samples were taken at 99°C and subsequently allowed to cool without mixing. It can be seen from Table I that, HMWSP A1 yields much smaller particle size compared to HMWSP A2 under identical processing conditions. The particle size and size distribution for HMWSP A1 are similar to those obtained for low density polyethylene studies previously [9]. We have shown that the emulsion particle size decreased

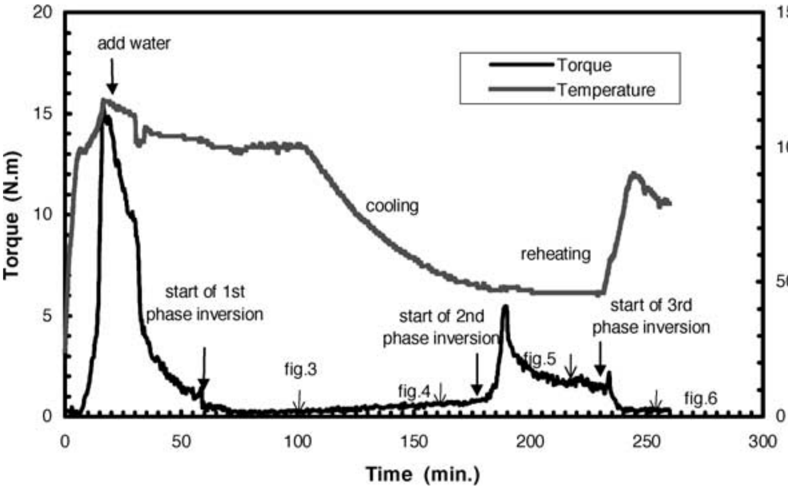


Figure 2 Phase inversion history of 80% EVA + 20% HMWSP-A1. The start of water addition and three phase inversions as well as the locations of samples for SEM examination are indicated. The first phase inversion took place after the addition of 20 wt% water into the system. The resulting [polymer melt-in-water] emulsion is diluted (to contain 30% water) while mixing, creating a [water-in-solid polymer] powdery dispersion. After cooling of this powder to 45°C, it is reheated while mixing. The third phase inversion starts when the temperature reaches ca. 48°C and a {[water-in-polymer melt]-in-water} type of multiple emulsion is obtained.

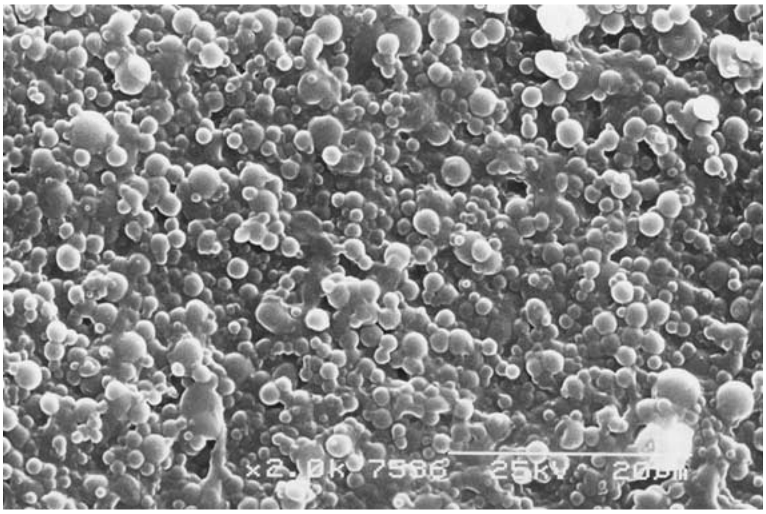


Figure 3 Scanning electron micrograph of latex obtained by phase inversion emulsification and subsequent dilution giving 30% water and 70% polymeric phase containing 80% EVA + 20% HMWSP-A1. The history of the emulsification is shown in Fig. 2. After the phase inversion from a [water-in-polymer melt] to [polymer melt-in-water] emulsion, the emulsion is diluted while mixing at 99°C for 30 minutes. The SEM sample was prepared by drying a drop of latex dispersion on a specimen mount followed by drying and carbon coating. The scale bar is 20 μm.

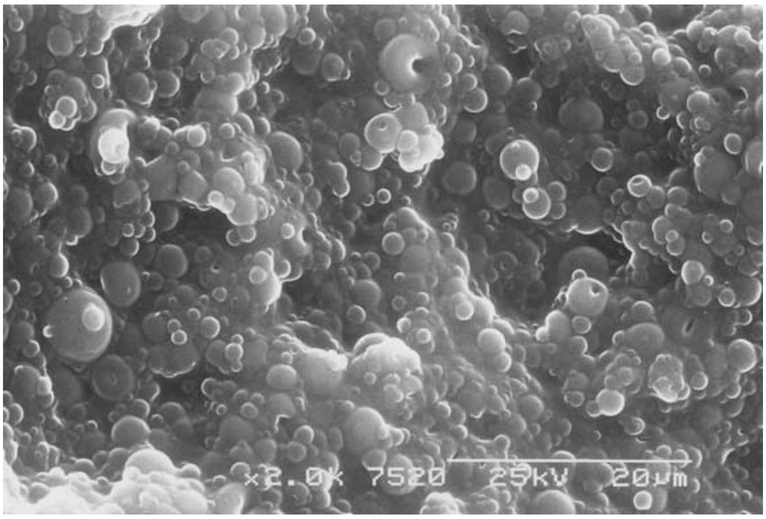
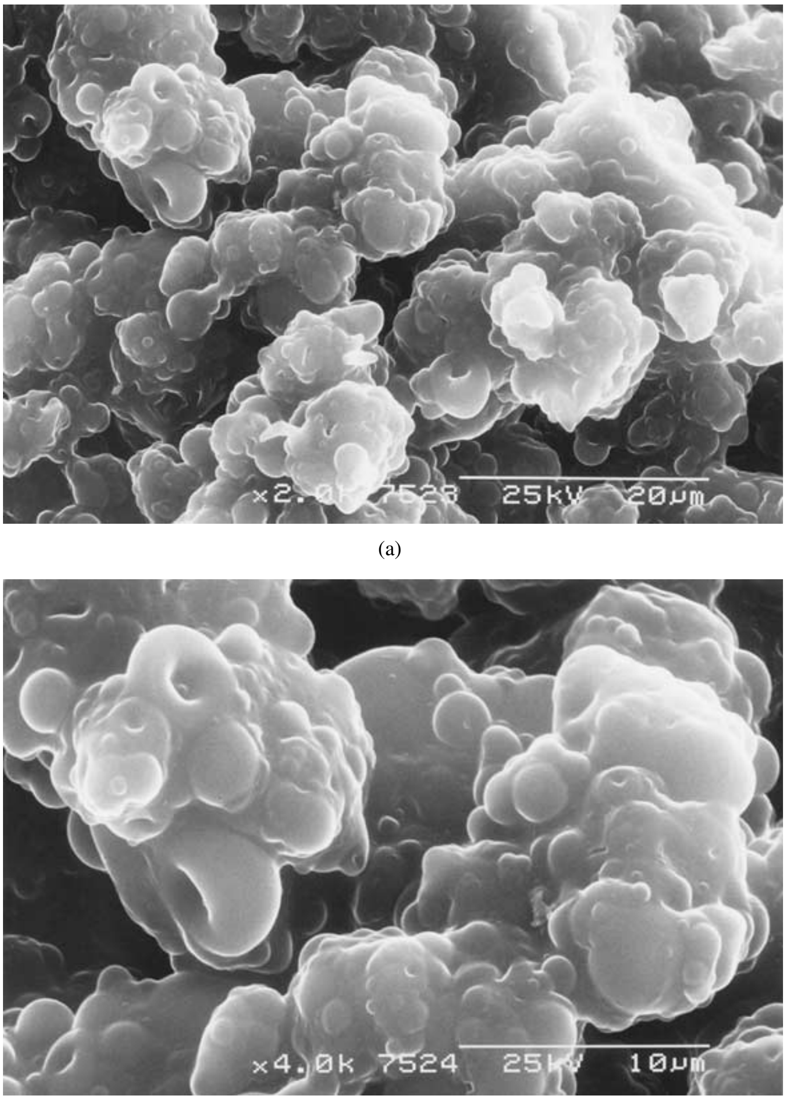


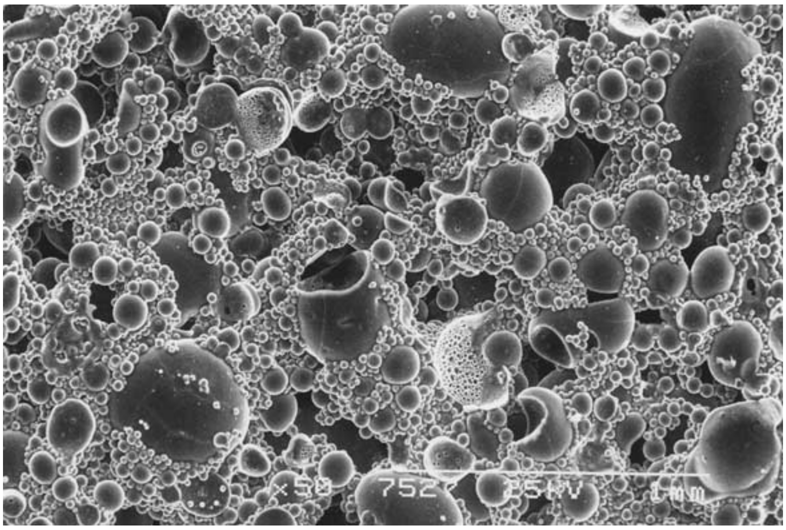
Figure 4 Scanning electron micrograph of the dispersion containing 80% EVA and 20% HMWSP A1 obtained after the second phase inversion when the [polymer melt-in-water] emulsion was cooled from 99°C to 45°C to yield a [water-in-solid polymer] powdery dispersion. This sample was taken when the temperature was 50°C, just before the formation of the powdery dispersion and therefore it does not show large scale aggregate formation. Scale bar is 20 μm.



(a)

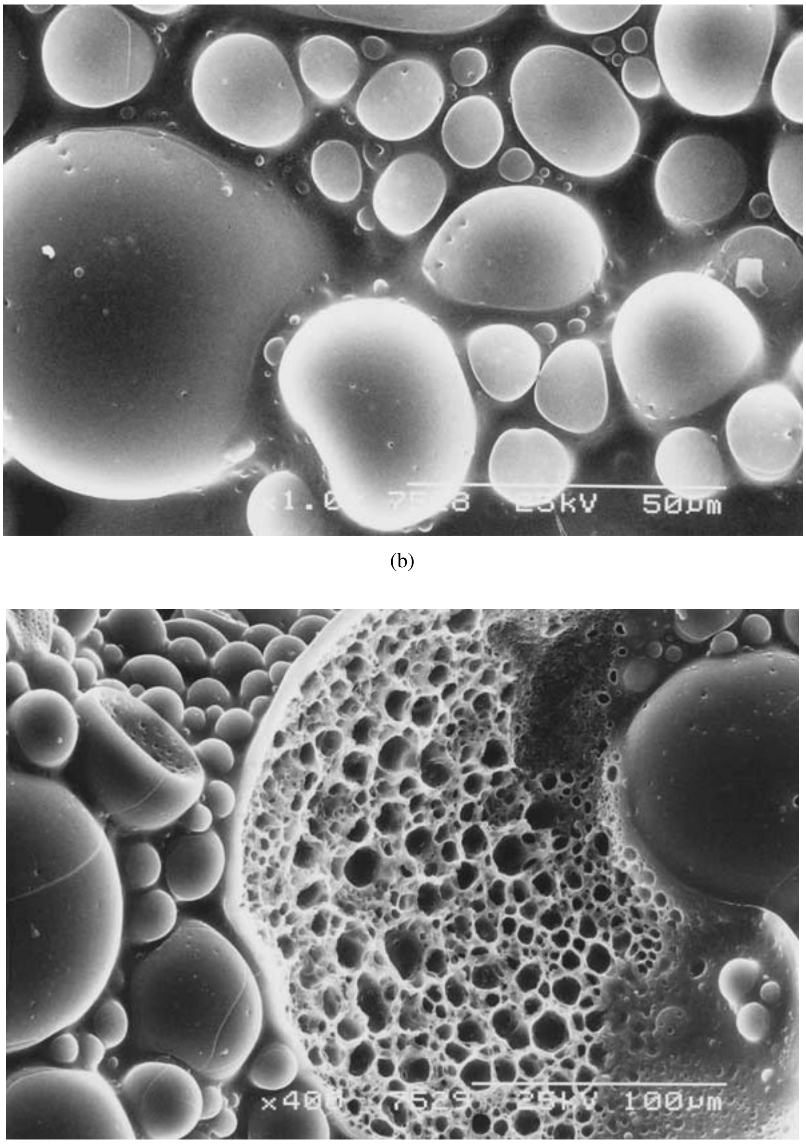
(b)

Figure 5 Scanning electron micrograph of the dispersion containing 80% EVA and 20% HMWSP A1 obtained after the second phase inversion when the [polymer melt-in-water] emulsion was cooled from 99°C to 45°C to yield a [water-in-solid polymer] powdery dispersion. Sample was taken when the second phase inversion had completed when temperature was 48°C during cooling. Originally the powder contained 30% water which was evaporated under vacuum for SEM examination. (a) Low magnification (scale bar 20 μm); (b) High magnification (scale bar 10 μm).



(a)

Figure 6 Scanning electron micrograph of the microporous particles (containing 80% EVA and 20% HMWSP A1) obtained after the third phase inversion in which a {[water-in-polymer melt]-in-water} type of multiple emulsion is first obtained and subsequently cooled to freeze the particle structure. (a) The general appearance of the dispersion showing the presence of different structures over a wide particle size range (scale bar 1 mm); (b) High magnification of (a), (scale bar 50 μm); (c) Presence of multiple emulsions (scale bar 100 μm).(*Continued.*)



(b)

(c)

Figure 6 (*Continued*).

with increasing HMWSP concentration. However, for a given surfactant/polymer system, there is always a minimum surfactant concentration present below which emulsification cannot be achieved. In the present case this minimum surfactant concentration was 15% for both HMWSP + EVA systems. However, it is clear that for EVA, HMWSP A1 should be used as preferred surfactant, if small particles are required. The dispersions are highly stable and particle size and size distribution change only slightly after 14 months of storage.

4. Conclusions

EVA latexes are prepared by phase inversion emulsification using hydrophobically modified water soluble polymers to provide the necessary surface activity. Under identical processing conditions, HMWSP A1 yields significantly smaller particle size ($D(v, 50)$ is more than ten fold smaller) compared to the case when HMWSP A2 is used. In fact the situation is reversed when low density polyethylene is emulsified using HMWSP A1 and A2. We note from the molecular structure of HMWSP A1 and A2 that HMWSP A1 is more hydrophobic (i.e., lower hydrophile–lypophile balance) compared to HMWSP A2. Considering that LDPE is more hydrophobic than EVA, surfactant choice may be made by considering the solubility parameter difference between the polymer and surface active material [21]. However, at this stage, there are not sufficient data available to warrant a correlation between droplet size and solubility parameter difference of the polymer and surface active material.

Similar to the emulsification of LDPE [9], EVA could not be emulsified if low molecular weight surfactants were used. After the phase inversion from a [water-in-polymer melt] emulsion to a [polymer melt-in-water] emulsion, at 20% water content, the emulsion needs to be diluted and cooled without mixing in order to prevent a phase re-inversion (second phase inversion). The latex size obtained for EVA is larger than that obtained for LDPE. This is in part due to the low viscosity of EVA melt which results in lower stresses for droplet break up.

After obtaining a [polymer melt-in-water] emulsion further mixing while cooling results in phase re-inversion forming a [water-in-polymer] even if the water content is above 20%. If the water content of this solid dispersion is 30%, a powdered material is obtained in which water is encapsulated by solid polymer. This powder can be dispersed in water and its apparent size is significantly larger than the latex particles obtained after the first phase inversion. These "powdery emulsions" can be used in powder coating.

Such powdery emulsions can be re-inverted back to [polymer-in-water] by heating the emulsion while mixing. This is termed as the third phase inversion. However, the particle size and size span are very large as observed from the SEM microphotographs. Furthermore, these emulsions contain multiple emulsions of the type [(water-in-polymer)-in-water]. This conclusion is reached from the examination of the SEM microphotographs of the dispersions obtained after cooling these emulsions. The observed phase inversions (first, second and third) are not sudden and they can be used in the preparation of latexes (first phase inversion). Microencapsulation of aqueous phases (second phase inversion) and finally the formation of microporous polymers (third phase inversion) provide additional product opportunities based on non-isothermal flow induced phase inversion. These last two polymeric structures are the result of the solidification of the polymer melts while mixing.

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