Particle Formation by Emulsion Inversion Method: Effect of the Stirring Speed on Inversion and Formation of Spherical Particles

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Summery: Phase inversion emulsification technique was employed in this work as a practical method to form epoxy particles. The effect of stirring speed on the inversion behaviour and the morphological aspects of the resulting solid epoxy particles are investigated. Emulsion inversion was induced by increasing the amount of initially dispersed deionized water in the presence of a non-ionic block copolymer surfactant at a fixed concentration. The process of inversion was followed by monitoring the variations in the rotational speed of the stirrer caused by the viscosity variations of the emulsifying system throughout the process. It was shown that the mixing speed plays an important role in controlling the size and size distribution of the resulting emulsion particles. Below a critical stirring speed, spherical particles could not be formed and the inversion process resulted in macroscopically non-homogeneous multi shape structures. Fully spherical particles were formed above this critical speed. Further increase in the rotational speed of the mixer, significantly reduced the size of these spherical particles with a wide and random size distributions controlled and considerably narrowed by the stirring speed. Dynamic light scattering analysis and scanning electron microscopy were used to study the particle size and size distributions. In addition, study of the rotational speed variations of the stirrer, which is directly related to the viscosity changes of the emulsifying system, revealed that a correlation between the physical aspects of the inversion behaviour and the viscosity changes during the emulsion inversion process could be established.

Keywords: epoxy resin; non-ionic emulsifier; phase inversion emulsification; spherical particles; stirring speed

Introduction

Water borne emulsions of polymer resins have received extensive attention in recent years since no environmentally harmful solvents are present in such systems. Different methods have been introduced for the preparation of the waterborne emulsions, most of them based on complex polymerization processes[1–2] or physical routes with low efficiency. Amongst different methods for the preparation of oil in water (O/W) emulsions, the emulsion inversion route has been known as a useful method especially for the emulsification of high viscosity materials such as epoxy resin. Moreover it has been proved that this method is highly effective in preparation of particles with pre-defined morphologies.[3] Emulsions are generally defined as metastable colloids made out of two immiscible fluids, one being dispersed in the other in the presence of a surface-active agent. Emulsion type, water-in-oil (W/O) emulsion or oil-in-water (O/W) emulsion, and emulsion stability are known to be associated with the phase behavior of the surfactant-oil-water systems.[4–6] Conversion between these two types of emulsions is generally called "phase inversion" or

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"emulsion inversion". The term "catastrophic phase inversion" was introduced by Salager[7] to describe inversion in emulsions induced by changes in the emulsion water-to-oil ratio, as opposed to transitional inversion induced by changing the surfactant affinity for the two phases. The term "catastrophic" was chosen after a suggestion by Dickinson[8,9] that the elementary catastrophe theory may be applicable to describe phase inversion in emulsions. This suggestion was based on the fact that emulsion phase inversion induced by increasing the volume fraction of the dispersed phase displays the qualitative characteristics of the so-called cusp catastrophe theory developed by Thom.[10] Further discussion in this article will be based on the premise that the employed emulsion inversion procedure is of catastrophic type regarding the above mentioned terminology. There are different parameters which control the physical aspects of the emulsion phase inversion process and the resulting particles: temperature, stirring speed, surfactant type, concentration, etc. However, experimental investigations verified that at definite experimental conditions (fixed temperature and emulsifier concentration), stirring speed is the most dominant parameter. It has been known that when surfactant reduces the interfacial tension in turbulent agitated liquid-liquid dispersions, drop break up generally occurs by mechanical energy rather than velocity or pressure fluctuations.[11] The Theory of drop deformation and break up by viscous shear was first formulated by Taylor[12] and further developed by others.[13–16] When the Capillary number defined by the ratio of viscous stress of the continuous phase, $\mu_c\gamma$, over the Laplace pressure, $2\sigma/d$, exceeds a critical value, drop deformation and break up occurs:

$$Ca = 2\mu_c\gamma d/\sigma \tag{1}$$

Where μ_c, is viscosity of the continuous phase, γ is the shear rate, σ is the interfacial tension and d is the drop diameter.[17] It could be seen that the higher the mechanical shear involved and the lower the interfacial tension, the greater is the ease of drop break up[18] and the smaller is the size of resulting drops.[19] However it is believed that increasing the stirring energy to infinity would result in the formation of some kind of molecular soup with extremely small drops of both phases in which case the continuous phase is the one whose drops coalesce more quickly.[20] In our previous study, we investigated the effect of the emulsifier concentration on the inversion behaviour of the epoxy resin and formation of spherical particles.[21] The aim of this study is to investigate such behavior in phase inversion emulsification as a complex, indirect emulsification route and to determine the extent of its influence on the resulting emulsions. The characterization of the phase inversion process and the investigation of the effective parameters such as stirring speed on the inversion behavior of such a highly viscous materials are scarcely reported in the literature but yet are urgently needed.

Experimental Part

The emulsion inversion experiments were carried out using a supported glass vessel (internal diameter 10 cm) and an anchor type agitator (diameter 9 cm) connected to a variable speed Heidolph RZR 2041. The stirring speed was initially set at 5 different rpms namely: 100, 300, 500, 1000, 1300 rpm (The resulting emulsions are indicated in this article by the numbers 1,2,3,4 and 5 respectively). All of the variations from these initial values caused by viscosity changes during the inversion process were recorded by the device. Bisphenol A epoxy resin, Epon 1001, with a weight average molecular weight of 1000, was purchased from Shell Co. and was used as received. The polymeric non-ionic emulsifier used, which is a block copolymer of ethylene oxide and propylene oxide, was obtained from Uniqema (SYNPERONIC PE/F108). This surfactant is in the solid form at room temperature with a melting point of 55 °C.

It contains 80% of ethylene oxide and has a molecular weight of 14926 g/mol. Micelle formation and interfacial properties of this surfactant type have been investigated elsewhere.[22,23] In all of the experiments, at the first step, the epoxy resin and the surfactant were mixed together at a constant emulsifier concentration of 5% (of the epoxy resin), above their melting temperature (75 °C), and then the phase inversion was brought about by the addition of deionized water to the system (increasing f_W) in a drop wise manner at a fixed rate of 80 drops/min (roughly equal to 3 mL/min) at the reaction temperature using a thermostatic pump. The phase inversions were indicated by measuring changes in the stirring speed of the stirrer from its initial value since as discussed in more detail in the results and discussion section, the inversion point is usually associated with a minimum in the viscosity of the emulsifying system. After completion of the emulsion inversion, where the mixing speed no more changes (in other words, when the viscosity of the emulsifying system becomes constant), more water was added in order to cool and dilute the inverted system. The morphology of the resulting particles was investigated by scanning electron microscopy. For preparation of the samples, in case of the emulsions with larger particles, the produced particles were separated using a conventional filter paper followed by the drying of the particles in a vacuum oven. The dried powders were then sputtered with Au on a metallic stub and were photographed using a Philips XL30 scanning electron microscope. In this case, the particle size measurement was carried out using SEM image processor. In the case of emulsions with fine particles, the droplet size was immediately measured after emulsification by using a SEMATech 630 dynamic light scattering (DLS) apparatus. For the SEM analysis of the produced particles in the case of fine emulsions, drops of the resulting emulsion were spread on a metallic stub followed by freeze drying of the samples.

Results and Discussion

General Description of the Emulsion Inversion Phenomena

As mentioned earlier, during the phase inversion period, the viscosity of the system changes, resulting in the variation of the rotational speed of the stirrer which was initially set at a specific amount (e.g. 1300 rpm for the emulsion No. 5). Figure 1 represents a typical example of such a reproducible relationship between the stirring speed and water volume fraction during the emulsion inversion process which was recorded by the stirring device. The rotational speed variation of the stirrer is inversely proportional to the viscosity changes throughout the inversion so that the increase of the stirring speed implies the reduction of the viscosity and vise versa. This is because the stirrer always exerts a constant amount of shear stress to the emulsifying mixture and as a result, the reduction/increase in the shear rate, which is directly proportional to the rotational speed of the stirrer, compensates for the increase/reduction in the viscosity of the system. Therefore one may observe the effect of addition of water to the surfactant/oil mixture as a function of rotational speed of the stirrer as we shown in our previous study.[21] The plots obtained were nearly analogous in shape with 4 distinguishable parts as indicated in Figure 1 (in order to demonstrate the parts more clearly, the plots obtained at other initial speeds which follow the same trend are not shown in this figure).

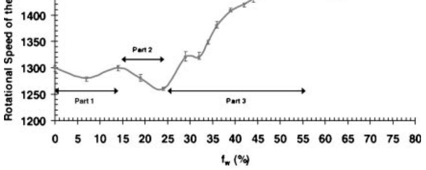

Figure 1.
Variations of the rotational speed of the stirrer with increasing water fraction during the emulsion inversion of the emulsifying system number 5.

The inversion point can be identified by the minimum in this curve (in the 2nd part) where the viscosity of the emulsifying system reaches a maximum. When water droplets are introduced to the system at the very initial steps of the experiment, the high viscosity continuous phase of the melted epoxy is mixed with adding water and efficiently disperses the water into small droplets via shear action and the surfactant. As the number of water drops increases, the interdroplet distance decreases, boosting the attractive interaction of the droplets which leads to the formation of a network, as described by Greiner and Evans [24]. The minimum observed in Figure 1 could be related to the network formation of water droplets. Upon addition of more water, new interfaces are generated, and redistribution of the block copolymer promotes coalescence of water droplets. Hence, the network is disrupted by coalescence into clusters, within which, due to the high water content, the phase inversion occurs. The presence of such a network has been confirmed from the conductivity curves obtained by Xu et al.[25] A short reproducible increase could be seen at the very initial part of the graph where the addition of water to the resin\surfactant mixture has just been started (the first part) indicating a sudden decrease in the viscosity of the emulsifying system. This could be attributed to the lubricating effect of water droplets before they could be dispersed completely in the continuous phase by the combined effect of the shear action and the surfactant. However, the behavior of the system during the 3rd part of the graph, where the phase inversion process promotes toward completion, is rather complicated and it may include numbers of local inversions[26] and formation of complex morphologies during this step as shown in Figure 2.

This Figure represents the SEM micrographs of some droplets taken from the system at the starting point of the phase inversion process of sample 5, i.e. at the beginning of the 3rd part in Figure 1. The particles shown in this Figure have an irregular cellular structure confirming the fact that the larger water domains formed initially inside the epoxy phase via the coalescence of the water drops before the inversion point have just started to join together. At this point, the observed structure breaks upon addition of more water to the system. This finally results in formation of discrete epoxy particles dispersed in a continuous water phase as shown in Figure 3B, C and D. This process is identified by a marked increase of the rotational speed of the stirrer (part 3) and formation of a plateau in the 4th part as could be observed in Figure 1.

The Effect of Stirring Speed

Table 1 summarizes the results of the particle size measurements of the emulsions inverted at 5 different stirring speeds.

When the stirring speed is too low, as it is the case for the emulsifying system number 1, with the rotational speed of

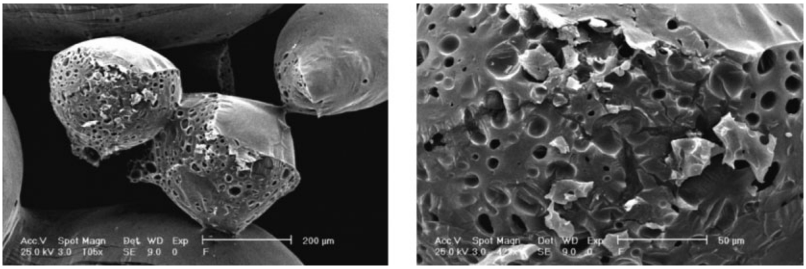

Figure 2.
SEM micrographs of the samples taken from the emulsifying system number 5, at the starting point of the inversion process.

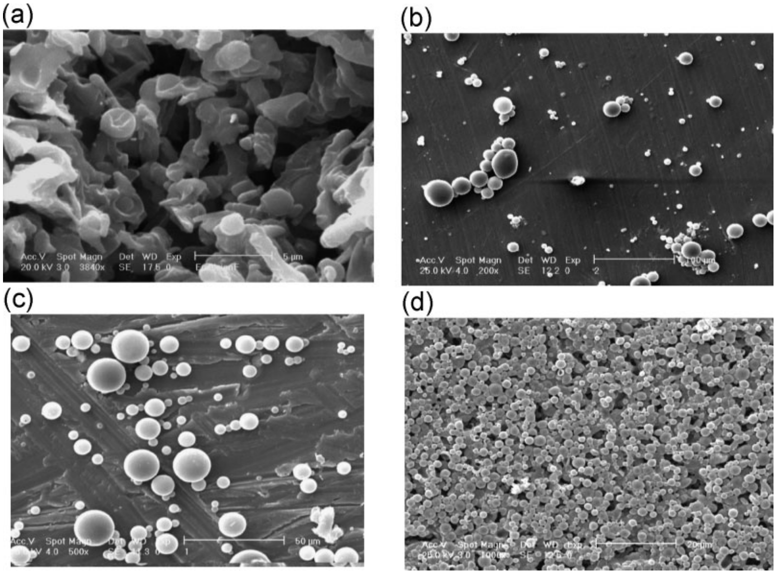

Figure 3.
SEM micrographs of the emulsion inversion products of the systems: A: No. 1 (stirring speed = 100 rpm), B: No. 2 (stirring speed = 300 rpm), C: No. 3 (stirring speed = 500 rpm) and D: No. 4 (stirring speed = 1000 rpm).

100 rpm, the mechanical energy applied to the mixture is not high enough to dominate the Laplace pressure effects (Equation 1). As a result, droplet formation is mostly hindered and the inversion process can just lead to the formation of a porous structure in which almost no separate particles are present as can be seen in the SEM micrograph shown in Figure 3A. In other words, in this case the emulsified system is characterized by a high degree of macroscopic lack of homogeneity with some segregated regions containing more water or more epoxy phase. When the mixing speed is increased to a greater value of 300 rpm as for the emulsifying system number 2, discrete epoxy particles will form, mostly having spherical geometry with an average particle diameter of 24.7 µm, as shown in Figure 3B. Such a stirring speed could be regarded as a critical one above which the phase inversion process results in the formation of emulsions of spherical epoxy particles. Increasing the rotational speed of the stirrer to 500 rpm, (sample No. 3) reduces the particle size of the dispersed droplets to nearly half of the previous value i.e. 12.7 µm. However, the greatest reduction in the particle size is observed when the stirring speed is doubled to 1000 rpm for the sample No. 4. Here, as shown in Table 1, the average particle diameter is reduced to

Table 1.
Results of the particle size measurements of the emulsified samples No.1-5 at the emulsifier concentration of 5%.

Emulsifying system No.	Stirring speed (rpm)	Average particle diameter (µm)	PDI	f_w at the inversion point (%)
1	100	–	–	Not detectable
2	300	24.6	1.46	19
3	500	12.7	1.28	19
4	1000	1.5	1.22	23
5	1300	1.2	1.41	24

1.5 μm with a particle size distribution remarkably narrowed by the stirring speed as shown in Figure 3C and 3D which is confirmed by the dynamic light scattering measurements given in Figure 4. This could be explained as follows: When the stirring is highly energetic, the drops and eddy scale are reduced and translational motion of surfactant is speeded up because surfactant diffusion from the bulk is partly substituted by convection, with a resulting quicker surfactant adsorption at the interface. A quicker surfactant adsorption means favoring formation of particles with mostly spherical morphology and narrower size distributions as could be observed in samples No. 4 and 5.

A simple reasoning could first lead to think that an increase in the stirring speed will always result in the particle size reduction, the trend which seems to be true up to this point. It is worth pointing out however that, although stirring can significantly reduce the droplet size of the emulsions by elongating the droplets before the breakage according to the rupture mechanism,[25] it also simultaneously increases the chance of the droplet coalescence by providing the inertia to gather the drops and by increasing the drop collision rate, although it has been known that the breakage mechanism is more favored when proper amount of emulsifier is used.[27] However, at sufficiently high stirring speeds, these two opposite effects balance each other and the particle size remains almost unchanged. This is what can be seen in Table 1, when the rotational speed of the stirring device is increased to 1300 rpm. As could be observed, the average particle size of the emulsifying system No. 5 has just slightly been reduced upon increasing the stirring speed to a relatively high value.

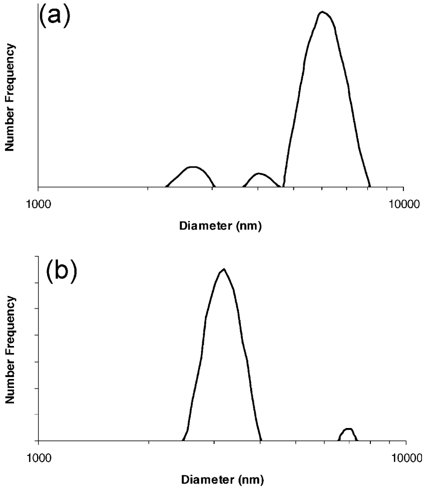

Figure 4.
Particle size distribution of the emulsification products of the systems: A: No. 4 and B: No. 5.

Conclusion

Stirring speed plays a substantial role in the emulsion inversion of high molecular weight epoxy resins. Under a critical stirring speed, when the mixing energy is considerably low, the produced shear is not sufficient to bend the interface one way or the other to form spherical particles. On the other hand, increasing the stirring speed above such a critical value makes it possible to produce perfectly spherical particles with their diameter significantly reduced upon increasing the rotational speed of the stirrer as confirmed by SEM micrographs and DLS analysis. However, at sufficiently high stirring speeds, the particle size of the droplets formed during phase inversion emulsification process seems to be almost independent of the stirring speed.

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