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Emulsion Phase Inversion of Epoxies with Non-ionic Block Emulsifiers: Effect of the Emulsifier Concentration on Inversion Phase and Formation of Spherical Particles

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A B S T R A C T

Phase inversion emulsification technique, as a versatile method for emulsification of high-viscosity materials has received considerable attention in recent years due to its potential for producing particles of precise geometries, sizes, and size distributions. This report involves an investigation on the effect of emulsifier concentration on the inversion behaviour and the morphological aspects of the resulting solid epoxy particles. Emulsion inversion was induced by increasing the amount of initially dispersed deionized water in presence of a non-ionic block copolymer surfactant. The process of inversion was followed by monitoring the changes in the rotational speed of the stirrer. These changes are introduced in this study as a means to probe the viscosity variations of the emulsifying system during the process. It is shown that under a specific emulsifier concentration mainly the rod-shaped and ellipsoidal particles are formed. The fully spherical particles, however, were formed above this specific concentration. Further increase in the emulsifier concentration significantly reduced the size of spherical particles, controlled, and narrowed their random size and wide distributions. Dynamic light scattering analysis and scanning electron microscopy were used to study the particles size and distribution. In addition, the study of rotational speed variations of the stirrer which is directly related to the viscosity changes of the emulsifying system revealed that during the inversion process a correlation could be established between the physical aspects of the inversion behaviour and the viscosity changes.

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INTRODUCTION

Water borne emulsions of polymer resins have received extensive attention in recent years due to absence of environmentally harmful solvents in such systems. Various methods have been introduced for the preparation of the water borne emulsions. These methods are mostly based on complex polymerization processes [1-2] or on some physical routes with low efficiency. Amongst the 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 resins.

Moreover, it has been proved that this method is highly effective for most polymers. The emulsions and particles produced in this way could be utilized in different areas such as paints, coatings, printing inks, cosmetics, enhanced oil recovery, polymeric concretes, and membranes [3-5].

Emulsions, generally defined as metastable colloids, consist of two immiscible fluids for one being dispersed in the other in presence of a surface-active agent. Emulsion type, i.e., water-in-oil (W/O) or oil-in-water (O/W), and emulsion stability are known to be associated with the phase behaviour of the surfactant-oil-water systems [6-8]. Conversion between these two types of emulsions is generally called phase inversion or emulsion inversion.

The term "catastrophic phase inversion" was introduced by Salager [9] to describe the inversion in emulsions induced by changes in emulsion water-to-oil ratio. This is opposite to that of transitional inversion phenomenon induced by a change in surfactant affinity for the two phases. The term "catastrophic" was chosen by salager after Dickinson [10,11] suggested that the catastrophe theory may be applicable to describe the phase inversion emulsions. This suggestion was based on the fact that emulsion phase inversion, induced by increasing the volume fraction of the dispersed phase, displays some qualitative characteristics of the so-called cusp catastrophe theory developed by Thom [12].

There are different parameters such as temperature, mixing speed, surfactant type, concentration, etc. which control the physical aspects of the emulsion phase inversion process and the resulting particles. However, elementary experiments have verified that the emulsifier type and concentration are the most dominant parameters.

The characterization of the phase inversion process and the investigation of the effective parameters on the inversion behaviour are scarcely reported in the literature and still further research in this area is greatly needed. The present article stands to explore this process further by studying the effect of non-ionic block copolymer emulsifier in the highly viscous system of epoxies.

EXPERIMENTAL

The emulsion inversion experiments were carried out using a supported glass vessel (internal diameter of 10 cm) and an anchor type agitator (diameter 9 cm) connected to a variable speed motor Heidolph RZR 2041 which was able to record the rpm changes of the stirrer. The stirring speed was set initially at nearly 1300 rpm. Bisphenol A epoxy resin, Epikot 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, SYNPERONIC PE/F108 was a triblock copolymer of PEO-PPO-PEO produced by Uniqema. This surfactant is in solid form at room temperature with a melting point of 55°C. The hydrophile lipophile balance number (HLB number) of this surfactant is about 15.7 at room temperature. Micelle formation and interfacial properties of this surfactant type have been investigated elsewhere [13,14].

In all the experiments, as the first step, the epoxy resin and the surfactant were mixed together at different surfactant concentrations namely 1.25, 2.5, 5, 10, and 15% of the polymeric surfactant (samples were indicated by the numbers 1, 2, 3, 4, and 5, respectively) above their melting temperature (75°C). Then, the phase inversion was brought about by dropwise addition of deionized water to the system (increasing f_w) at a steady rate of 80 drops/min. (about 3.2 mL/min) at the reaction temperature using a thermostatic pump, ERWEKA EM 702.

The phase inversions were indicated by measuring the changes observed in the initial mixing speed of the stirrer. After completion of the emulsion inversion, where the mixing speed does not change anymore (in other words, when the viscosity of the emulsifying system stays constant) more water was added in order to cool and dilute the inverted system. It should be mentioned that the amount of epoxy resin used was kept the same, i.e., 15 g for all samples.

The morphology of the resulting particles was investigated by scanning electron microscopy. For this, in case of the emulsions with larger particles, the produced particles were separated using a conventional filter paper followed by drying 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 a SEM image processor. In the case of emulsions with fine particles, the droplet size was measured immediately after emulsification by using a SEMATech 630 dynamic light scattering apparatus (DLS). For the SEM analysis of the produced particles in case of emulsions with fine particles, one drop of the resulting emulsion was spread on a metallic stub followed by freeze drying the sample using a ZIRBUS 37539 freeze drier.

RESULTS AND DISCUSSION

General Description of the Emulsion Inversion Phenomenon

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 speed.

Figure 1a represents the relationship between the stirring speed and water volume fraction during the emulsion inversion process at four different emulsifier concentrations (samples 2-5), recorded by the stirring device. The rotational speed variation of the stirrer is inversely proportional to the viscosity changes throughout the inversion. Thus, an increase of the stirring speed implies a reduction in the viscosity and vise versa. It is in this way that 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 [9].

As could be seen in Figure 1a, the obtained curves generally exhibit an almost "S" shape with four distinct regions. The inversion point can be identified by a minimum point in the curves (in the 2nd region) where the viscosity of the emulsifying system reaches a maximum.

When water drops are introduced into the system at the very initial stages of the experiment, the highly viscous continuous phase of the melted epoxy is
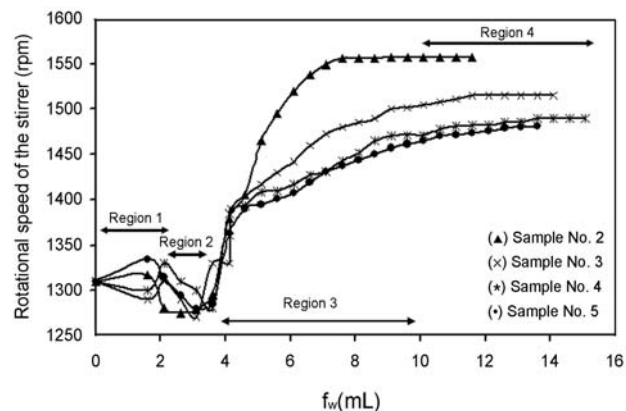

(a)
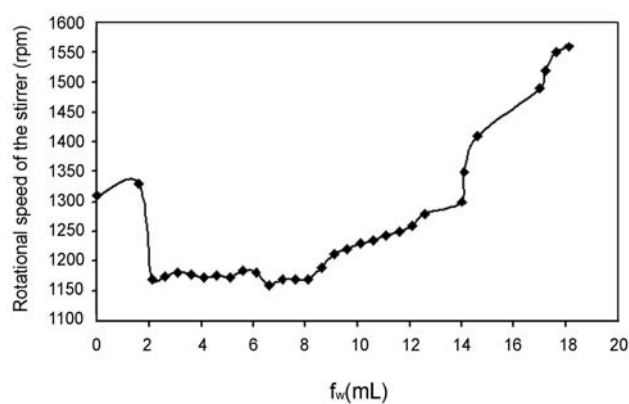
(b)

Figure 1. Variations of the rotational speed of the stirrer with water volume fraction for (a) samples No. 2-4 and (b) sample No. 1.

mixed with water added to the surfactant/oil mixture at a relatively high shear stress which it efficiently disperses the water into small droplets. As the number of water droplets increases, the interdroplet distance decreases, thus, the attractive interaction of the droplets leads to the formation of a network as described by Greiner and Evans [15]. The minimum observed in Figure 1a may be related to such a network formation of water droplets.

Upon addition of more water, new interfaces are generated, and redistribution of the block copolymer surfactant promotes the coalescence of water droplets. This may cause the disruption of the existing network and the coalescence of the particles into clusters which extends into high water content, where the phase inversion occurs. The presence of such a network has been confirmed by the conductivity curves

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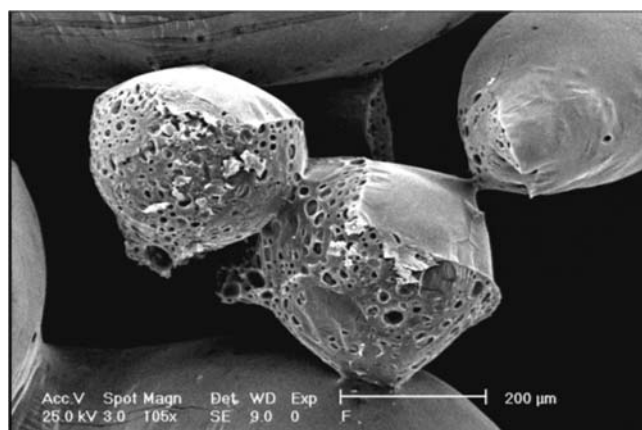
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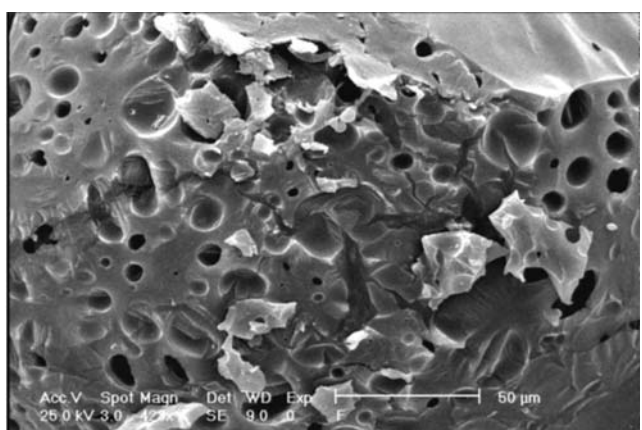
(b)

Figure 2. SEM Micrographs of the droplets taken during the inversion process of sample No. 3 at f_w =3.5 mL (the magnifications are: (a) ×150 and (b) ×423).

obtained by Xu et al. [16]. Before the completion of the emulsion inversion process and during the increase in rotational speed of the stirrer, the inversion point in the 3rd region of the curve is observed. As it is not possible to measure the dynamic viscosity accurately during this fast phase inversion where the dynamic viscosity might have changed almost 5 or 6 times, at this stage we cannot explore the Winsor ratios for the system and make a contribution solely on the physical formation of perfectly spherical particles of epoxies.

The behaviour of this complex system is not always clear and may include numbers of local inversions [16]. The complex morphologies are shown in Figure 2. This Figure represents the SEM micrographs of some droplets taken from the system during

the phase inversion process of the sample No. 3, just after the inversion point (the 3rd region) at f_w = 3.5 mL. 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 water droplets have just started to join together before the inversion point. At this point, the observed structure breaks upon addition of more water to the system. This would finally result in formation of discrete epoxy particles dispersed in a continuous water phase as shown in Figure 3. This process is identified by a marked increase in the rotational speed of the stirrer (region 3) and formation of a plateau in region 4 as could be observed in Figure 1a.

**The Effect of Surfactant Concentration**
The overall trend is observed in Figure 1a after the completion of the inversion process. The rotational speeds recorded at the plateau (the 4th region) decrease with increasing the emulsifier concentration as shown in Figure 1a. This may imply that upon formation of a larger quantity of smaller spherical particles, the emulsifier increases the viscosity of the system. The SEM micrographs of the produced particles which are shown in Figure 3 prove this fact.

As it is observed in Figure 3a, when the surfactant concentration is too low (sample No. 1) the interfacial film absorbed at the interface between the two phases is not wide enough to embrace the fine particles with larger surface areas [17]. This may result in the formation of very large particles with diverse geometries which frequently include more oval and rod shaped particles and less the spherical ones. In such a way, the produced suspension is so unstable that the suspended particles would immediately deposit at the bottom of the reaction vessel in the absence of the mixing.

The rpm variations vs. water volume fractions during the inversion of such a system are depicted in Figure 1b. This curve indicates a significantly wide inversion area consisting of many local inversions occurred almost all over the experiment. The reduction in the viscosity of the system gradually continues towards a final abrupt change leading to an unstable suspended system with a considerably low viscosity which is due to the large particle size of the droplets,
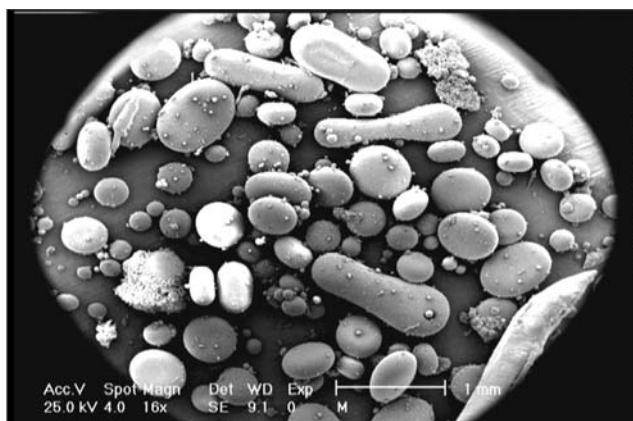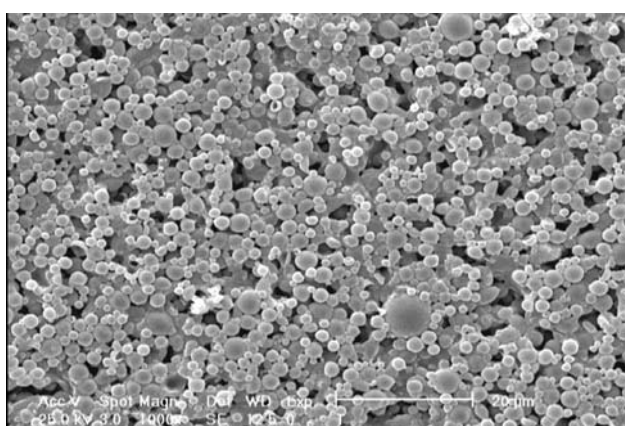
(a)
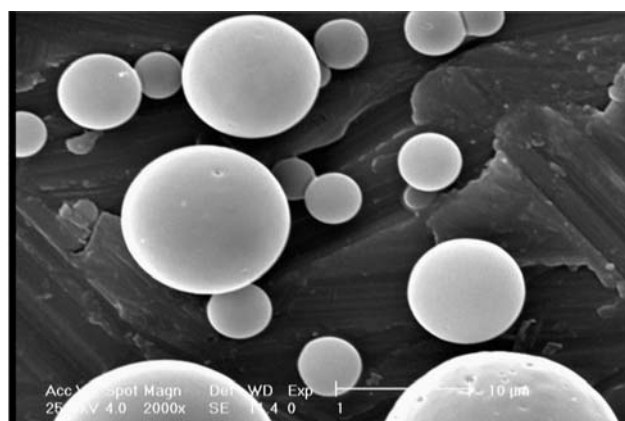
(c)
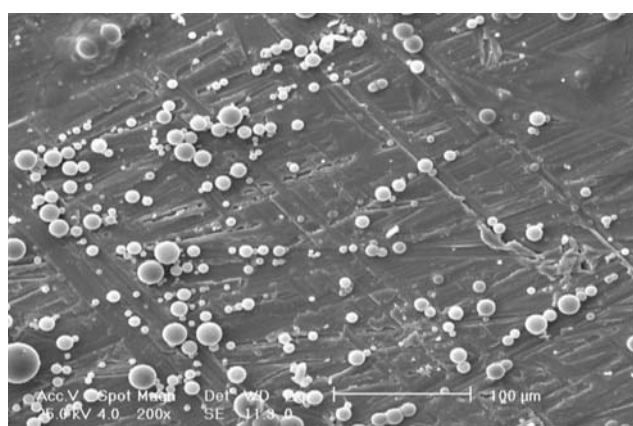
(b)

(d)

Figure 3. SEM Micrographs of the particles produced by the emulsion inversion of: (a) sample No. 1 (mag. = ×16); (b) sample No. 2 (mag. = ×200); (c) sample No. 3 (mag. = ×2000) ; (d) sample No. 5 (mag. = ×1000).

as stated before. Increasing the emulsifier concentration resulted in the formation of smaller particles with the spherical geometry. The typical morphology of the particles produced at higher concentrations (sample No. 2) can be seen in Figure 3b. Upon further addition of the emulsifier concentration, the particle size of forming droplets decreases significantly until the formation of sub-micron size particles. Figure 3d shows that increasing the emulsifier concentration would also narrow the size distribution of the droplets. Such a reduction is confirmed by dynamic light scattering results of the samples No. 4 and 5 as shown in Figure 4.

According to the obtained results, the mean diameter of the emulsion particles of the samples No. 4 and No. 5 are 604 and 434 nm, respectively. Changing the emulsifier concentration would also alter the emul-
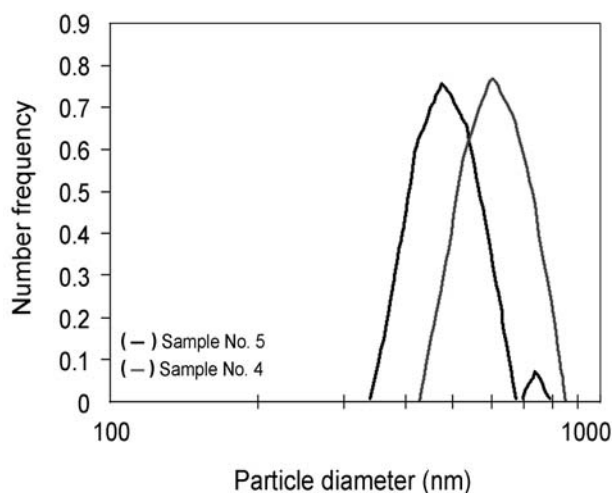

Figure 4. DLS Results of the particle samples No.4 and No.5.

sion inversion point (the minimum in the plots of Figure 1a). As could be observed in this figure, the emulsifier concentration increases the water fraction at the inversion point. The exact reason for such behaviour has not yet been completely elucidated. However, it is probably due to the enhanced dispersibility of the water phase at higher emulsifier concentrations where a thicker interfacial film formed by the emulsifier around the water droplets increases the resistance of the dispersed water droplets toward coalescence. This finally increases the amount of water required to initiate the inversion process of the initial W/O emulsion.

CONCLUSION

Emulsifier concentration plays a substantial role in the emulsion inversion of high molecular weight epoxy resins. Increasing the emulsifier concentration will remarkably reduce the size and particle size distribution of the resulting O/W emulsions as confirmed by SEM micrographs and DLS results. The rotational speed of the stirrer is introduced in this article as a useful probe for the investigation of emulsion inversion process in terms of the inversion evolution stage and even the particle size of the resulting emulsions. It is possible to make perfectly spherical sub-micron particles with a diameter of 604 and 434 nm in a very clean and high conversion process in which we can control not only the size and distribution of the particles but also their transformations into other geometries and shapes.

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