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Biobased Surfactant as a Colloid Stabiliser in 50% Zinc Dibutyldithiocarbamate Dispersion

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Recent development in surfactant technology has made it possible to produce surfactants based on plant extracts. A new material based on polyfructose extracted from roots of chicory was used as a stabiliser in 50% ZDBC dispersion and the properties were evaluated and compared with other systems. Although results of the light scattering technique did not show much difference in the particle size, a marked difference in the particle shape was observed when Transmission Electron Microscopy (TEM) was used. TEM micrographs of ammonium caseinate stabilised dispersion showed formation of uneven, saw like shaped particles with a wide particle size distribution whereas polyfructose stabilised dispersion showed formation of very even, circular shaped particles with a narrow particle size distribution. Viscosity results of polyfructose stabilised dispersion showed a pseudoplastic behavior similar to normal dispersion systems. Although a hard sediment formed with ammonium caseinate stabilised dispersion, no caking was observed in the polyfructose stabilised dispersion.

Key words: surfactant; polyfructose; dispersions; particle size; sedimentation

In dry rubber technology, the use of chemicals such as vulcanising agents, activators and accelerators are important in order to enhance the properties of rubber. Such use of chemicals is also done for natural rubber latex but with some changes. Instead of using dry powders, the chemicals are first dispersed in water using appropriate machinery as the chemicals are water insoluble. Apart from the use in latex, dispersions are also extensively used in other technologies such as in the paints, pigments, printing inks and plastics industry.

For the purpose of using in natural rubber latex, the chemicals are usually mixed with water and surfactants (small amounts of a dispersing agent and colloid stabiliser). The slurry is then ground in a suitable grinder for an appropriate length of time to produce a dispersion with a particle size of less than 5 μm[1]. The dispersing agents used are usually of the anionic type whereas the colloid stabilisers are usually the water soluble plant hydrocolloids, proteinaceous substances, water soluble cellulose derivatives or starches.

Of many, one particular colloid stabiliser of interest is casein. Casein, being a proteinaceous substance, is produced through isolation from cow's milk. Unlike stabilisers from plants (plant hydrocolloids), casein is not affected by

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the changes due to weather. Casein, in its soluble form (ammonium caseinate) not only acts as a colloid stabiliser but also as a deflocculating agent for certain chemicals such as sulphur and dithiocarbamate accelerators.

Recently, much attention is being made towards stabilisers obtained from sugars. One such material is based on a polyfructose extracted from the roots of chicory (*Chicorium intybus*). The polyfructose, known as inulin is a polydisperse polysaccharide consisting mainly, if not exclusively, β (2→1) fructosyl fructose units (Fm) with one glucopyranose unit at the reducing end (GFm)[2].

In this paper, we report the effects of using Inutec® SP1 as a colloid stabiliser in 50% zinc dibutyldithiocarbamate (ZDBC) accelerator dispersion. The particle size, viscosity, sedimentation rate and microscopy were studied and the results were compared with similar dispersion of different formulations containing ammonium caseinate with bentonite clay as thickener.

MATERIALS AND METHODS

Materials

Perkasit ZDBC was purchased from Flexsys N.V/S.A., Belgium, the dispersing agent (Anchoid®) was obtained from Castle Chemicals Limited, U.K. whereas the bentonite clay was from Sud Chemie, Germany. The colloid stabilisers, casein and polyfructose (Inutec® SP1) were supplied by a local company and Orafti Bio Based Chemicals, Belgium, respectively. The composition and specification of both casein and polyfructose have been reported elsewhere[3,4].

Methods

Preparation of samples. For the purpose of preparing the 50% ZDBC dispersions, the formulations as shown in *Table 1* were used. Ammonium caseinate was prepared from casein using a method reported elsewhere[5]. The chemicals (ZDBC, Anchoid®, ammonium caseinate, polyfructose and bentonite clay) were first mixed together in a beaker until homogenous. Distilled water was added next and the mixture was stirred again before being transferred into a ball mill and milled for 48 hours. The resulting dispersions were then analysed for their particle size, viscosity, sedimentation rate and morphology.

Characterisation

Particle size. A SALD-2001 SHIMADZU Laser Diffraction Particle Size Analyzer was used to measure the particle size of the dispersions. About 0.5 mL of dispersion was pipetted into a beaker containing 200 mL of distilled water and stirred. The resulting mixture was further diluted until 1% and transferred to the sample bath before obtaining the results using the SALD-2001 v1.0 measuring software.

Viscosity. About 400 mL of dispersion was first poured into a beaker. Brookfield Viscometer Model LVT equipped with spindle no. 2 was used to measure the viscosity. The final viscosity measurement of the dispersion was taken from the average of two duplicates.

Sedimentation rate. About 100 mL of dispersion was carefully poured into a volumetric cylinder. The reduction in volume of the surface of the dispersion was measured for 5 days. The reduction in volume *versus* time graph was plotted and the slope was

TABLE 1. FORMULATIONS USED FOR PREPARING 50% ZDBC DISPERSIONS

Chemicals	Weight of Formulations (g)				
	1	2	3	4	5
100% ZDBC	50	50	50	50	50
100% Dispersing agent[a]	2	1	1	1	1
10% Ammonium caseinate	-	10	-	10	-
10% Polyfructose[b]	-	-	10	-	10
100% Bentonite clay	-	-	-	1	1
Distilled water	48	39	39	38	38
Total	100	100	100	100	100

[a]Anchoid®
[b]Inutec® SP1

taken as the sedimentation rate of the dispersion.

Microscopy. About 1 µL of dispersion was pipetted into a microcentrifuge tube containing 1 mL of distilled water. The microcentrifuge tube was capped and the content homogenised using a vortex mixer. The resulting dispersion was picked up using a copper wire loop at which it was dried before being deposited onto a formvar coated nickel grid. Micrographs of the samples were viewed using a Philips CM12 TEM at 80 kV and the digital images captured using the analySIS® imaging software (Soft Imaging System GmbH, Germany).

RESULTS AND DISCUSSION

Surfactants are materials which preferentially concentrate at interfaces[6], therefore bringing marked differences in the surface properties of liquid media[7] through reduction of its interfacial tension. In dispersions, surfactants adsorb onto the surface of solid particles, affecting the stability of particles through numerous ways[8]. However, during the dispersion process, the formation of aggregates or agglomerates complicates the adsorption of surfactants onto the particles as a dispersion is only complete when individually suspended particles are obtained. Therefore, mills such as the pebble or attritor mills are used to break the aggregates or agglomerates and also grind them to reduce the particle size.

In this study, five ZDBC dispersions were prepared with different formulations (*Table 1*). Of the five formulations, Formulation 1 was used as the control. It consisted of ZDBC, water and a dispersing agent, Anchoid® which is a condensation product of naphthalene-2-sulphonic acid and formaldehyde[8]. The structure is such that the dispersing agent has a hydrophilic backbone with hydrophobic side groups. The colloid stabilisers used in Formulations 2, 3, 4 and 5 were ammonium caseinate and polyfructose. Amonium caseinate which is primarily casein[9] is built of spherical aggregates of several casein molecules held together by hydrophobic bonds and salt bridges. On the other hand, the polyfructose is a hydrophobically modified inulin surfactant produced through grafting several alkyl groups on the inulin backbone. Formulation 4 and 5 consists of similar formulations with addition of bentonite clay as a thickener. Milling was performed in a pebble mill for 48 hours at 70 r.p.m. and the results of particle size after milling is as shown in *Figure 1*.

From the results, it was observed that grinding reduced the particle size of ZDBC dispersions to less than 2.5 µm. The addition of colloid stabilisers (Formulation 2 and 3) further reduced the particle size of dispersion when compared to the control (Formulation 1). As the milling time for every formulation was similar, it would suggest that the stabilisers prevented the particles from forming aggregates, in other words, more particles were dispersed as individual particles. The addition of bentonite clay did not affect the particle size of ammonium caseinate stabilised dispersion (Formulation 4) but a slight increase in the size of particles was observed for the polyfructose stabilised dispersions (Formulation 5).

As for the particle size distributions (*Figure 2*), a shift from broad (Formulation 1) to a slightly narrow (Formulations 2 – 5) distribution occurred. The addition of colloid stabilisers resulted in a more homogenous bell shaped distribution of the dispersion particles (Formulation 2 and 3). The incorporation of bentonite clay in Formulation 4 shifted the distribution to the left suggesting formation of smaller dispersion particles when compared to Formulation 2. However, the opposite was observed when bentonite clay was incorporated into the dispersion containing polyfructose (Formulation 5) suggesting formation of larger dispersion particles compared to Formulation 3 as evident from *Figure 1*.

As observed earlier (*Figure 1*), dispersion particle size reduces with milling. The reduction of larger particles into many smaller

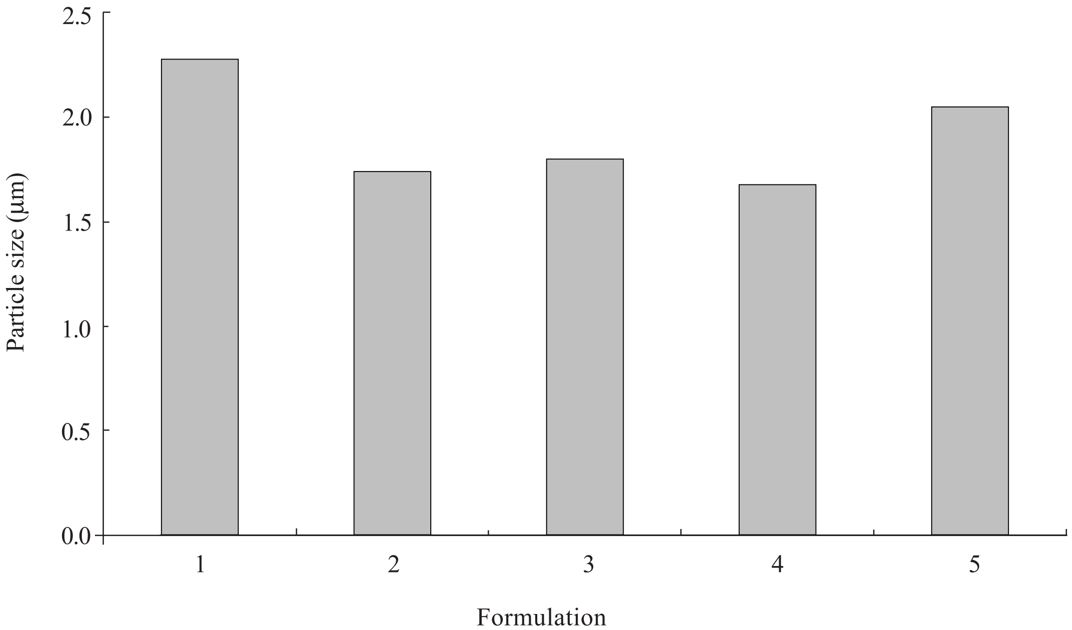
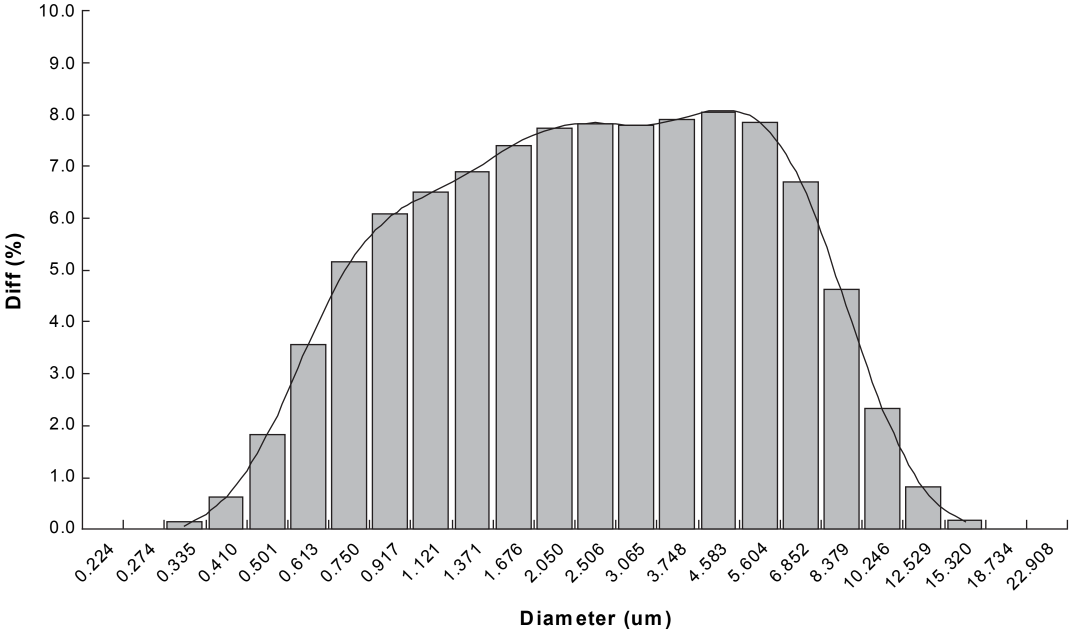
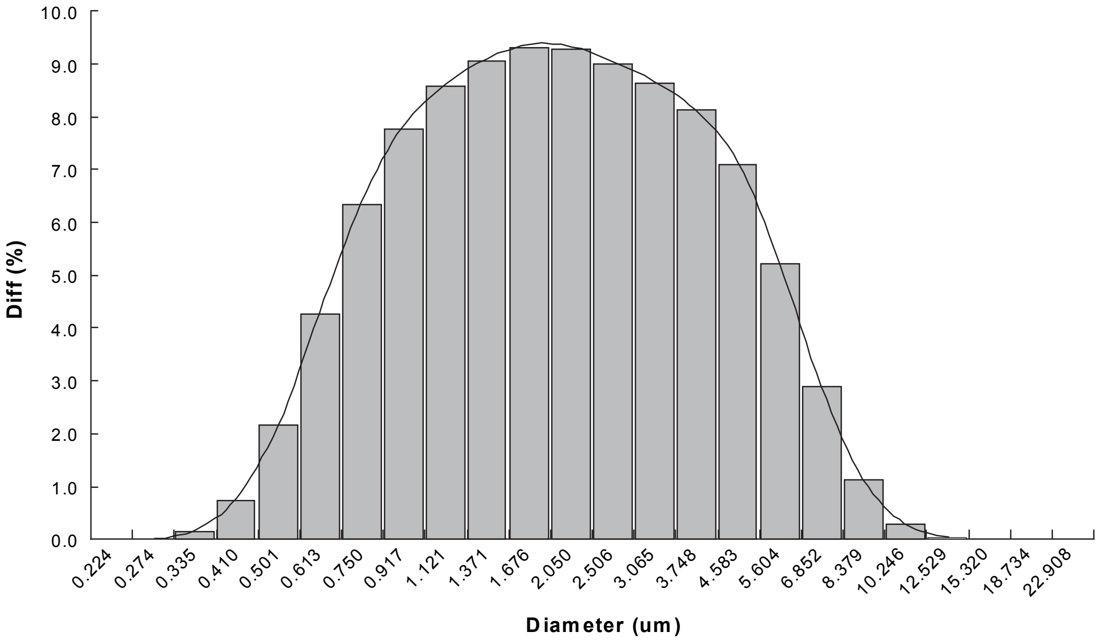


Figure 1. The average particle size of ZDBC dispersions from different formulations.

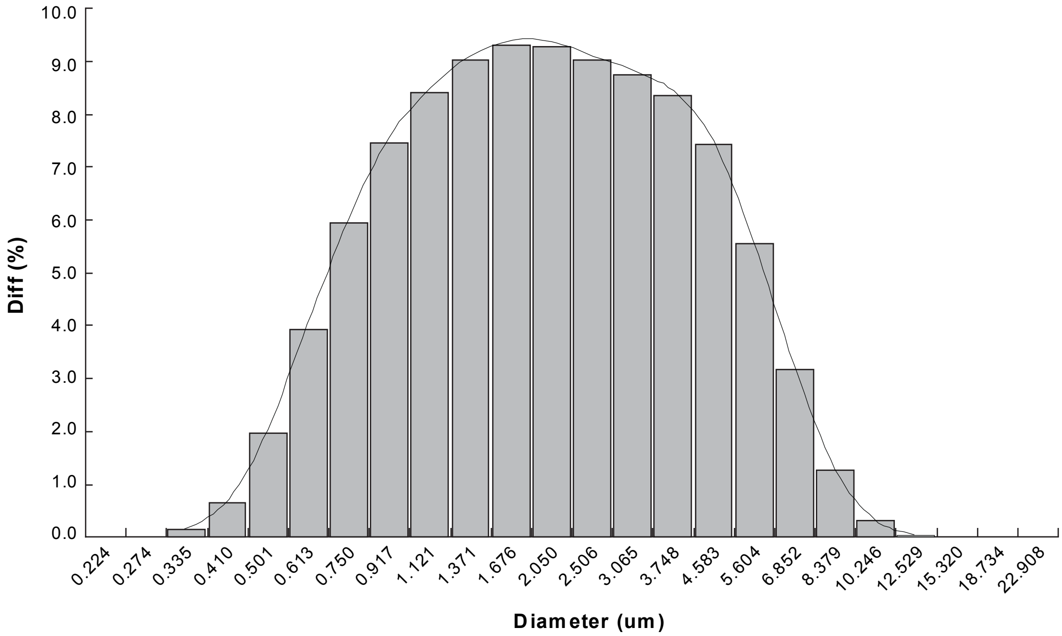


(a) Formulation 1

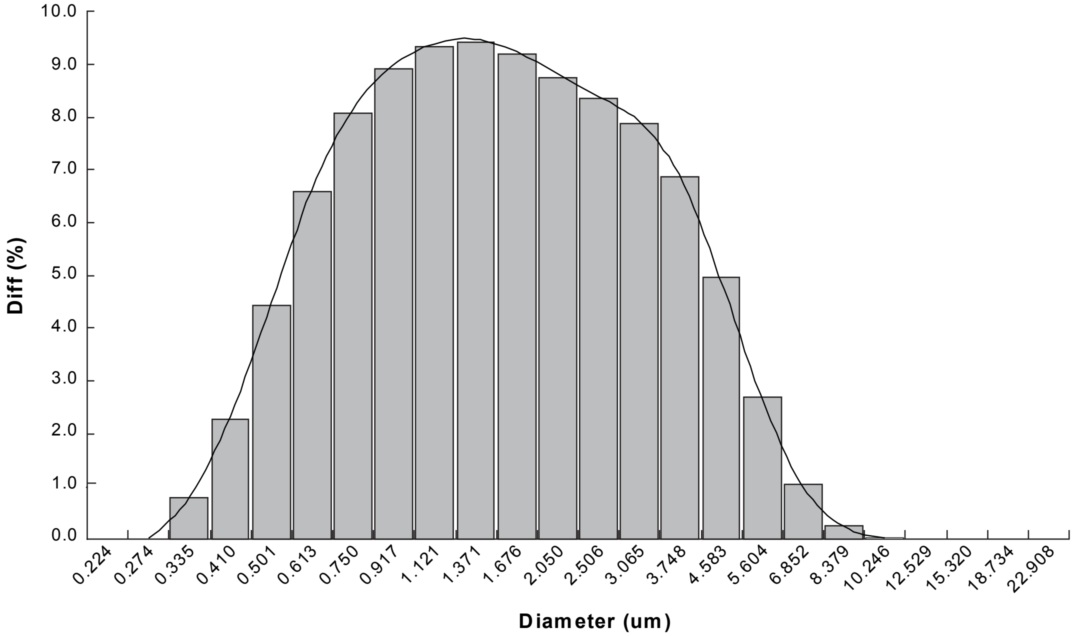


(b) Formulation 2

Figure 2. (cont'd)

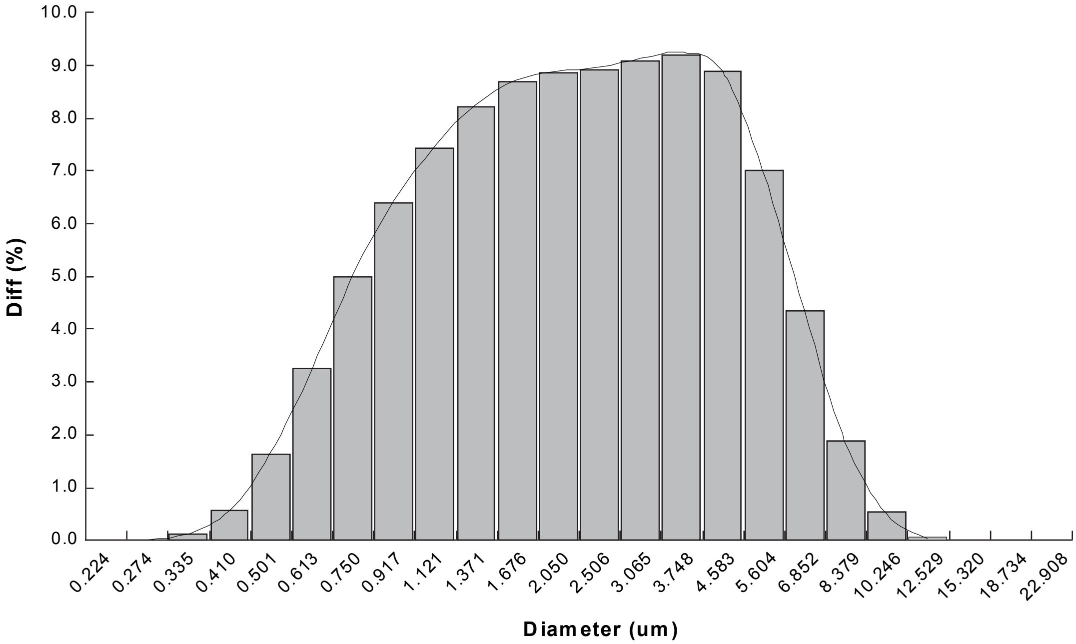


(c) Formulation 3



(d) Formulation 4

Figure 2. (cont'd)



(e) Formulation 5

Figure 2. Particle size distribution of ZDBC formulations.

fractions would therefore affect the viscosity of the final dispersions. In *Figure 3* the effect of shear rate on the apparent viscosity of ZDBC dispersions is shown. Here, the term apparent viscosity is used because the dispersion behaves as a non – Newtonian fluid[10]. Furthermore, the viscosity depends on the force required to move the different size of particles available in the dispersion. From the results, it is observed that the dispersions behave in a pseudoplastic manner in which the apparent viscosity decreases with increasing shear rate. According to Moudgil and coworkers[11], at lower shear rates, the apparent viscosity of a dispersion tends to be significantly higher due to immobilised liquid but as the shear rate increases, the flocculates are broken down and the entrapped liquid is released, hence a reduction in viscosity is observed.

It is also evident from *Figure 3* that formulations containing colloid stabilisers showed a different viscosity behavior compared to the control (Formulation 1). The change in the viscosity of dispersions could be due to the individual or combined effect of the dispersing agent and colloid stabiliser. In the control (Formulation 1), the dispersing agent plays an important role by adsorbing onto the ZDBC particles through its hydrophobic side groups during the milling process. The incorporation of ammonium caseinate and polyfructose adds more surfactant into the already surfactant containing environment. Since caseinate is mobile on oil – water interface[12], it is possible that it not only stabilises the dispersion but also causes thinning of the aqueous phase which results in the reduction of dispersion viscosity. On the other hand, slight increment in the viscosity occurred when polyfructose was used which could probably be a result of additional anchoring of alkyl chains of polyfructose onto the dispersion particles.

Though so, the opposite was observed when the experiments were repeated without ZDBC (*Table 2*). Formulation 2 containing ammonium caseinate showed slightly higher apparent viscosity compared to Formulation 3 which contained polyfructose. The sudden change in the viscosity profile as evident from *Table 2* compared to the results in *Figure 3* could have probably been due to the structural makeup of the stabilisers. Compared to the polyfructose which is hydrophobically modified by introducing several alkyl chains onto its main body[4], the casein used to produce ammonium caseinate is a globular protein, heterogenous in nature and composed of molecules synthesised through condensation of free amino acids[3]. In other words, casein has a polypeptide structure with its molecular weight ranging from 33 600 to 375 000 whereas the polyfructose has a molecular weight of around 4 700. These characteristics would possibly be involved in determining the viscosity behavior observed in both systems, with (*Figure 3*) and without ZDBC (*Table 2*).

The addition of bentonite clay (*Figure 4*) increased the viscosity of the dispersions to more than six times when compared with the control. Having a bundle like plate structure and on addition into water, the sodium ions on

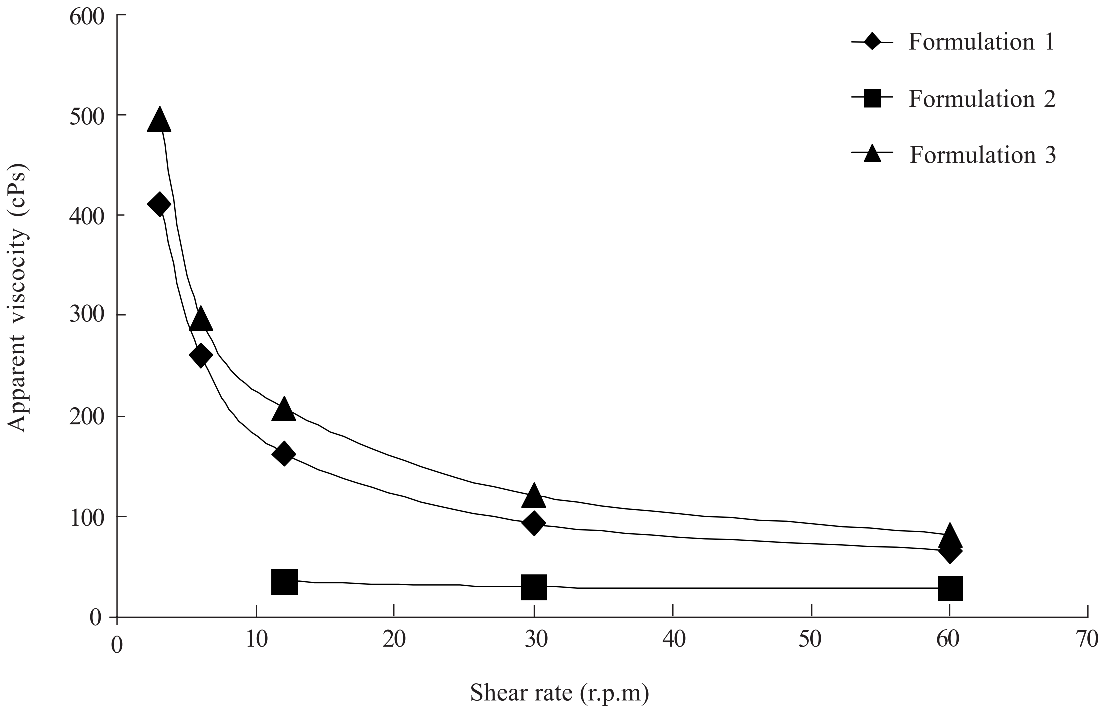


Figure 3. Apparent viscosity of dispersions with and without colloid stabilisers.

TABLE 2. THE APPARENT VISCOSITY OF SURFACTANT SYSTEMS*

Formulations	Shear rate (r.p.m)				
	3	6	12	30	60
	Apparent viscosity (cPs)				
1	NM	NM	NM	4.0	3.5
2	NM	NM	NM	5.0	3.8
3	NM	NM	NM	3.3	2.8

*Average of three readings.
NM: Not Measurable

the surface of bentonite clay[13] hydrates and causes negative charges to be generated which repels each other. As a result, the clay swells and the viscosity of the dispersions increases.

It is important that dispersions produced through milling do not settle and sediment during storage. However, this is not entirely possible because most dispersions would either form a cream or sediment with time. For this study, the sedimentation rates of dispersions were measured and the results are as shown in *Table 3*. The highest sedimentation rate of 1.5 mL/day was recorded for dispersion of

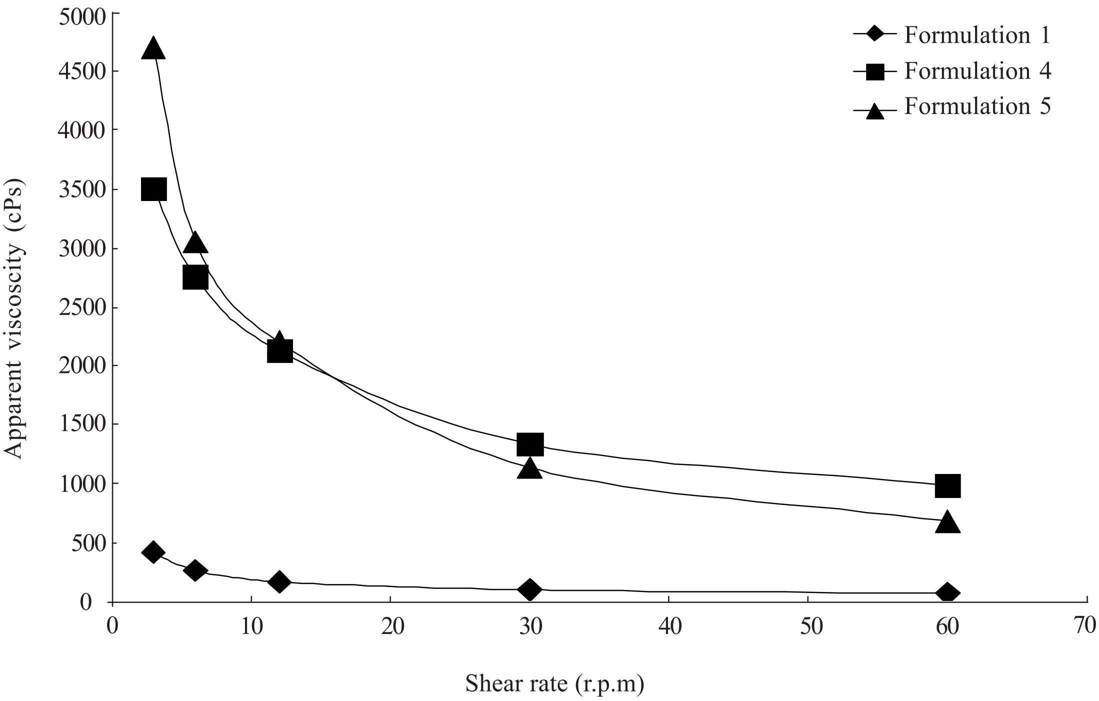
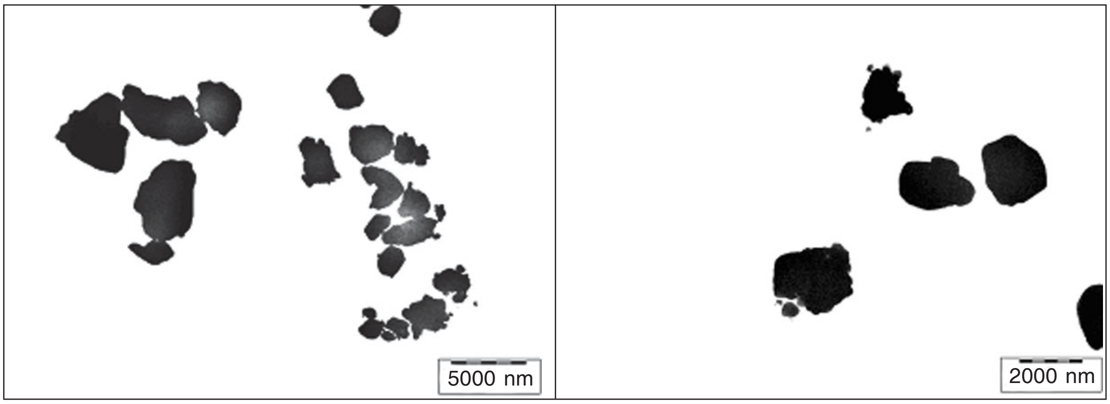


Figure 4. Effect of bentonite clay on the apparent viscosity of dispersions.

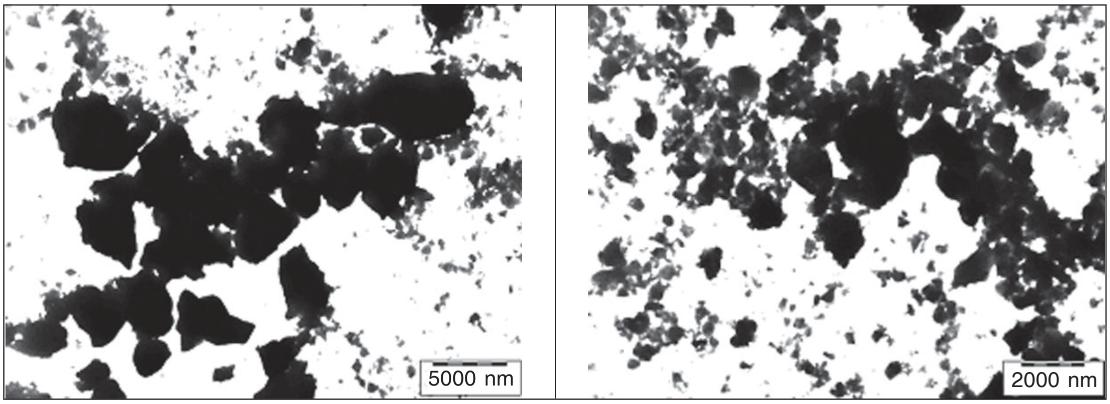
Formulation 1



Magnification 2650x

Magnification 5600x

Formulation 2



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Formulation 3

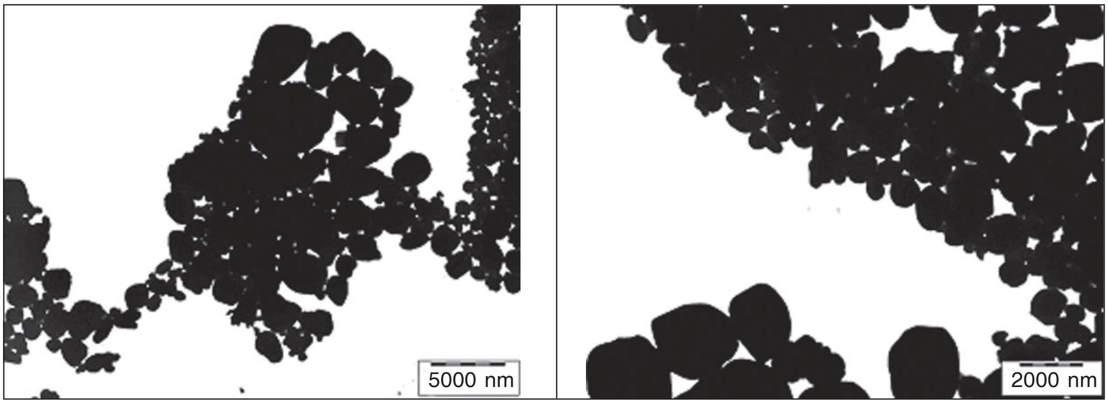

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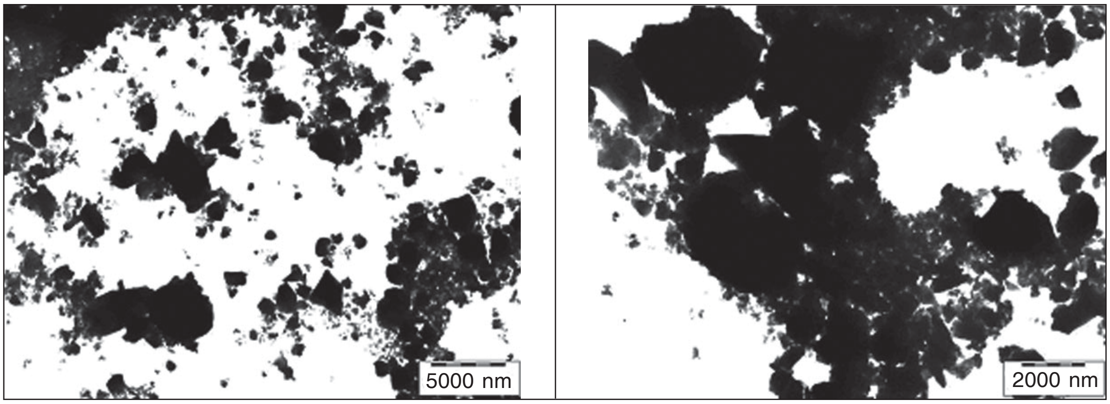
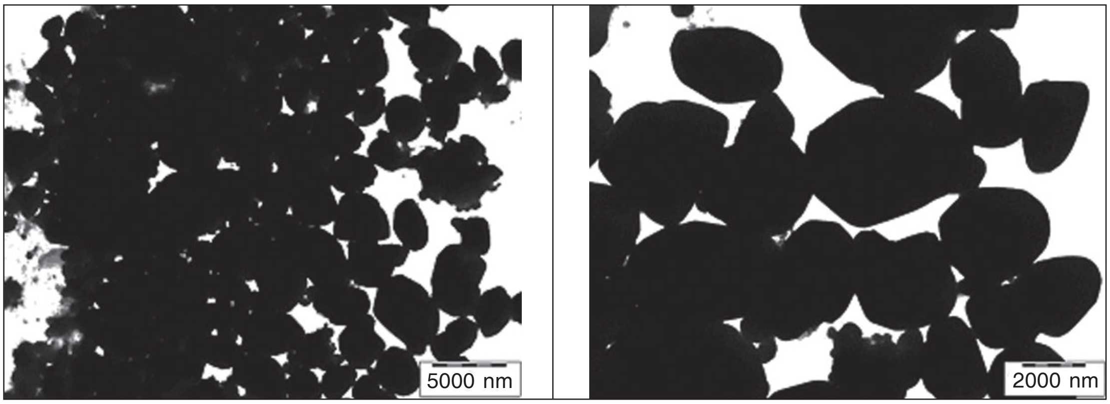
Figure 5. (cont'd)

Formulation 4



Magnification 2650x | Magnification 5600x

Formulation 5



Magnification 2650x | Magnification 5600x

Figure 5. Micrographs of dispersions from different formulations observed using TEM at magnifications of 2650x and 5600x.

Formulation 1. The addition of colloid stabilisers significantly reduced the sedimentation rates to less than 0.5 mL/day. However, the addition of bentonite clay in Formulation 4 and Formulation 5 did not affect the sedimentation rate. Although colloid stabilisers reduced the sedimentation rates, a different behavior was observed from dispersions of Formulation 2 and 3. A hard cake was formed at the bottom of the container for dispersion of Formulation 2 which could probably be due to casein aggregation leading to gel formation as explained by Walstra[9]. On the other hand, no caking was observed for dispersion of Formulation 3. Furthermore, the sediment could also be easily re-dispersed with slight stirring.

Figure 5 shows the micrographs of dispersions with different formulations. As observed, dispersions of Formulations 1, 2

TABLE 3. SEDIMENTATION RATES OF DIFFERENT ZDBC FORMULATIONS*

Formulations	1	2	3	4	5
Sedimentation rate (mL/day)	1.5	0.4	0.5	0.4	0.5

*Average of three readings.

and 4 gave irregular individual particles with a broad range of particle sizes. Due to this, caking was observed as a result of sedimentation. On the other hand, very fine, homogenous spherical particles with a narrow particle size distribution were obtained with Formulation 3 and 5. It is possible that a flocculated, network structure between the particles was formed which contributed to the loosely packed, easily re-dispersible sediment as observed from the micrographs of Formulations 3 and 5.

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