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Title

Optimisation and analysis of bead milling process for preparation of highly viscous, binder-free dispersions of carbon black pigment

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Abstract

Lab scale milling equipment is often employed to prepare dispersion formulations that possess considerably different characteristics from each other. The viscosity of a pre-mixed dispersion is one of the main parameters to consider when selecting a particular milling equipment for grinding of pigment. Generally, high viscosity dispersions are not easy to grind using a lab-scale re-circulating bead mill. There are numerous factors that can potentially result in changes in the starting point formulations. It is therefore crucial to assess any variations in the pigment loading occurring during milling for extended time periods. In this study, rheological characterisation, thermogravimetric analyses and surface resistivity measurements have been carried out on multiple dispersion formulations and it is shown that pigment loading after milling can be different from that in the starting point formulation.

Highlights

1. A method to effectively grind very high viscosity pre-mixed dispersions of carbon black on a bead mill.
2. A method to ascertain the effectiveness of a bead milling operation for preparation of high viscosity dispersions.
3. A general method that can be employed to ascertain the repeatability of milling operation for various dispersion systems.

Keywords

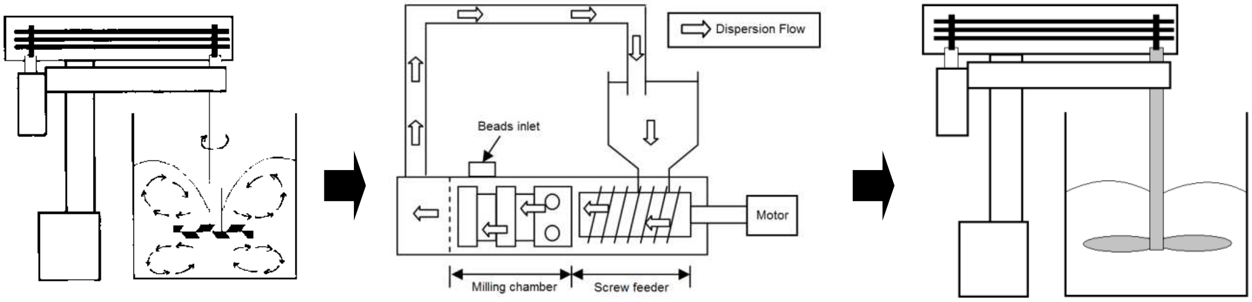
Waterborne coatings, bead milling, dispersion formulation, pigment loss, carbon black.

Abbreviations

DOWP	**Amount of dispersant (gm) on the weight of pigment**
OAN	**Oil absorption number**

1. Introduction

The property requirements for various coating systems are often significantly different from one another (1). Thus, the technological aspects of the corresponding production processes are also different. A typical coating production process involving bead milling is depicted in Figure 1. However, there are huge varieties of manufacturing equipment that are designed to meet specific requirements of a specific coating manufacturing process. The selection of equipment and the sequence of the steps that are involved in preparation of a coating system are primarily dependent on the type of coating and the quantities being manufactured (2). In addition, the important factors pertaining to the formulation include the viscosity of the premix, the vehicle, the solids content in the formulation, the pigment hardness, temperature limitations, aeration tendencies and so on (3). The main target to be achieved in a coating manufacturing process is proper blending of all of the formulation components, in general, and an optimal dispersion of the pigment, in particular. Detailed accounts of the mechanisms involved in dispersing a pigment are reported in literature (4-6).



Milling (Bead milling)

Pre-mixing

Let-down

Figure 1: Typical steps involved in manufacturing of a pigmented coating system (7)

Depending upon the design of milling equipment, single or multiple passes through a mill may be required to achieve the required reduction in particle size, a narrow particle size distribution and to improve stability (8-10). It is important to note that the main manufacturing cost in coating preparation is associated with the cost of pigment milling which has two components. One is the cost that is associated with the duration of the milling which in turn dictates the total energy that is consumed during the process (11). The other component of cost is associated to the wear and tear on the milling equipment. The wear of the conventional ceramic or metallic grinding media needs to be considered as this can lead to contamination of the dispersion (12-15). The optimum milling process parameters, i.e., the milling time and the milling speed, to prepare pigment dispersion depends on a number of factors including the pigment hardness, the pigment aggregate size, the solubility of pigment in the dispersion medium, the effectiveness of the dispersant(s) and the design of the milling equipment (16-19). Mathematical models have also been developed to identify, predict and optimise the most significant pigment grinding parameters (20-21).

As new applications of coatings are envisaged, increasing numbers of pigments are employed as functional materials (22-23). As a result, a coating system manufacturer has to frequently deal with formulations that possess significantly different characteristics from each other. In many cases, the cost of pigment is a major consideration due to which the coating manufacturer is faced with the challenge of maximising the desired functionality while using an optimally low amount of the pigment. The optimum amounts of all of the other formulation ingredients also have a direct influence on the properties of the end product. In addition, it is crucial to assess the capabilities and limitations of the available milling system for each unique type of formulation. This is commonly done by preparing a series of dispersions using lab scale milling equipment followed by characterisation of the same using a number of techniques such as electrophoresis, rheological assessments, particle size analysis, sedimentation tests and adsorption isotherm (24-28). Another technique called electroacoustics allows zeta potential measurement in concentrated suspensions (29-31). In order to speed up the formulation optimisation and characterisation processes, in-situ and online analytical techniques have been reported recently (32-34).

It is clear from a review of the available literature that a significant number of studies report on the analysis of dispersion preparation process and characterisation of dispersions. However, there is a clear need to devise a method to estimate any potential changes in the starting point formulation that can occur during the dispersion preparation process, particularly during milling. This is considered to be important and thus the focus of this work because not all pigment milling equipment designs provide air-tight environment and as a result the vehicle (dispersion medium) can evaporate during milling for extended time periods. If the viscosity of a premixed dispersion is high then the loss of vehicle can accelerate due to increased temperatures. In addition, pigment loss can possibly occur in the form of accumulations in various sections of the milling equipment, particularly during the first several minutes of milling if the dispersion flow characteristics are not ideal (shear thinning). The aforementioned potential problems are more likely to occur in lab-scale milling equipment which is often used to grind pre-mixed dispersions possessing significantly different rheological characteristics. This can lead to changes in the starting point formulations and subsequently unexpected product performance. In this work, a simple method is proposed to estimate the optimum milling duration and at the same time record any changes in the starting point formulation in terms of pigment loading.

2. Materials and Methods

2.1 Pigments

Carbon blacks of the same particle morphology may vary considerably in their ease of dispersion. Such differences in dispersibility can be attributed to the amount of chemisorbed complexes. On the basis of a consideration of this property, carbon black pigments that contained low volatile matter content were selected for this study. Some of the more important characteristics, as provided by the suppliers of these pigments, are provided in Table 1. In order to put more strain on the milling process, binder-free, waterborne dispersions of these pigments were prepared.

Table 1: Specifications of carbon black pigments (as provided by the suppliers)

Pigment (Supplier Code)	**Supplier**	**BET Surface area (m^2/g)**	**OAN ($cm^3/100g$)**	**Volatile content (%)**
Vulcan XC605	Cabot	59	148	< 0.1
Ensaco 250G	Timcal	62	191	0.2

2.2 Dispersants

For the dispersion and stabilisation of non-polar pigments such as carbon black, high molecular weight dispersing additives are generally recommended. In this situation, steric hindrance becomes the primary mechanism by means of which pigment particles are stabilised in the dispersion medium. The more important characteristics of the selected dispersants are provided in Table 2.

Table 2: Dispersants used and their characteristics (as provided by the suppliers).

Dispersant	**Supplier**	**Water solubility**	**Active Matter (wt%)**
Solsperse 44000	Lubrizol	Soluble	50
BYK-190	BYK Chemie	Completely miscible	40
Tego Dispers 760W	Evonik Tego	> 500 g/L	35

2.3 Preparation of dispersion

Prior to studying the effectiveness of the bead mill and its ability to handle high viscosity pre-mixed dispersions, the optimum dispersant dosage for each of the pigments was determined using a high throughput process as described in a previous work by one of the authors (35). The sequence of steps followed to prepare dispersions of carbon black for the present study is depicted in Figure 2. A high-speed over-head stirrer with a dissolver type blade was used for high shear pre-mixing while the bead mill used was a Mini 50 Motormill manufactured by Eiger Torrance Limited. Two batches, each of 100 gm, of the pigment-dispersant combinations tabulated in Table 3 were prepared and analysed. This provided an opportunity to establish the repeatability of the process.

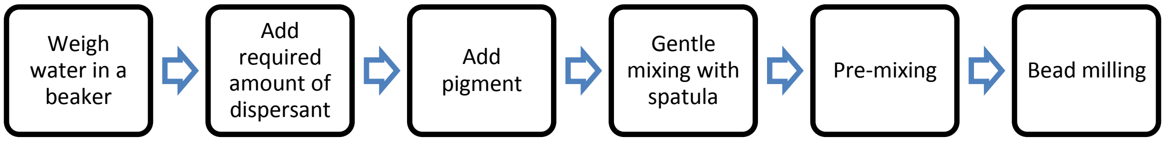


Figure 2: Sequence of addition of formulation ingredients and the steps involved in milling of dispersions

Table 3: Pigment-dispersant combinations prepared in the present study

	DISPERSANT		
PIGMENT	**Solsperse 44000 (Dispersant1)**	**BYK-190 (Dispersant2)**	**Tego 760W (Dispersant3)**
Vulcan XC605 (Carbon1)	Carbon1-Dispersant1	Carbon1-Dispersant2	Carbon1-Disperssant3
Ensaco 250G (Carbon2)	Carbon2-Dispersant1	Carbon2-Dispersant2	Carbon2-Dispersant3

In some trial runs, it was observed that milling speed in the range of 3750-4000 RPM resulted in improved recirculation of the pre-mixed dispersions. This range of milling speed is also in line with the manufacturer's recommendation to minimise any wear and tear of the equipment. The size of zirconium oxide beads used as grinding media was between 1 – 1.25 mm and the bead loading was maintained between 30 – 35 mL.

3. Analytical Techniques

3.1 Rheological characterisation

The viscosity of a dispersion ($\eta_{dispersion}$) is mainly dependent on the particle size, size distribution and the solids concentration (volume fraction, $\emptyset$). The nature of inter-particle forces also has a considerable effect. In a system of monodisperse spherical particles, the increase in viscosity with solids loading is generally accepted to be given by the Krieger-Dougherty equation:

$$\eta_{dispersion} = \eta_{medium}\left[1-\frac{\emptyset}{\emptyset_m}\right]^{[-\eta]\emptyset_m}$$

Where $\emptyset_m$ is the maximum packing fraction obtainable, which for monodisperse spheres is equal to random close packing, i.e. 0.64. $[\eta]$ is the intrinsic viscosity which for spherical particles is 2.5, and η_{medium} which in this case is the viscosity of water. In other words, addition of particles to a suspension increases the viscosity until at the maximum packing fraction the viscosity tends to infinity.

This was done using a TA Instruments AR-1500 EX rheometer. ASTM D4287-00(2010) standard method was used for measuring high shear viscosity using a cone-and-plate configuration. A 60 mm stainless steel cone with 1° taper angle and 27 μm truncation gap was used. A continuous ramp test was employed and the viscosity profile was recorded over a shear rate range of 1 s^{-1} to 1000 s^{-1}.

3.2 Surface resistivity measurements

For surface resistivity measurements, dispersions samples were collected at regular intervals during milling. Drawdowns of collected dispersion samples were produced on standard proofing paper using hand coater apparatus (K-bar No. 3) and surface resistivity was measured after 24 hours of drying in ambient conditions (21 – 24 ^{o}C). The surface resistivity of a 3 cm x 3 cm area of the drawdown was measured and five measurements were taken for each sample.

3.3 Thermogravimetric analysis (TGA)

In most cases, the pre-mixed dispersions were very viscous and it was difficult to ensure proper recirculation, especially during the initial several minutes of bead milling. As mentioned in the prior text, this created potential chances of changes in the starting formulation due to accumulation of pigment in various sections of the mill or due to evaporation of a significant amount of water (dispersion medium). Thus, the pigment loading of each batch of a milled dispersion was determined. For this purpose, thermogravimetric analysis of both batches of each dispersion formulation was carried out in order to determine the solids content at the end of milling process. The analysis was performed using a TA Instruments TGA Q50 and the parameters that were set for this purpose are tabulated in Table 4.

Table 4: TGA parameters for dispersion analysis

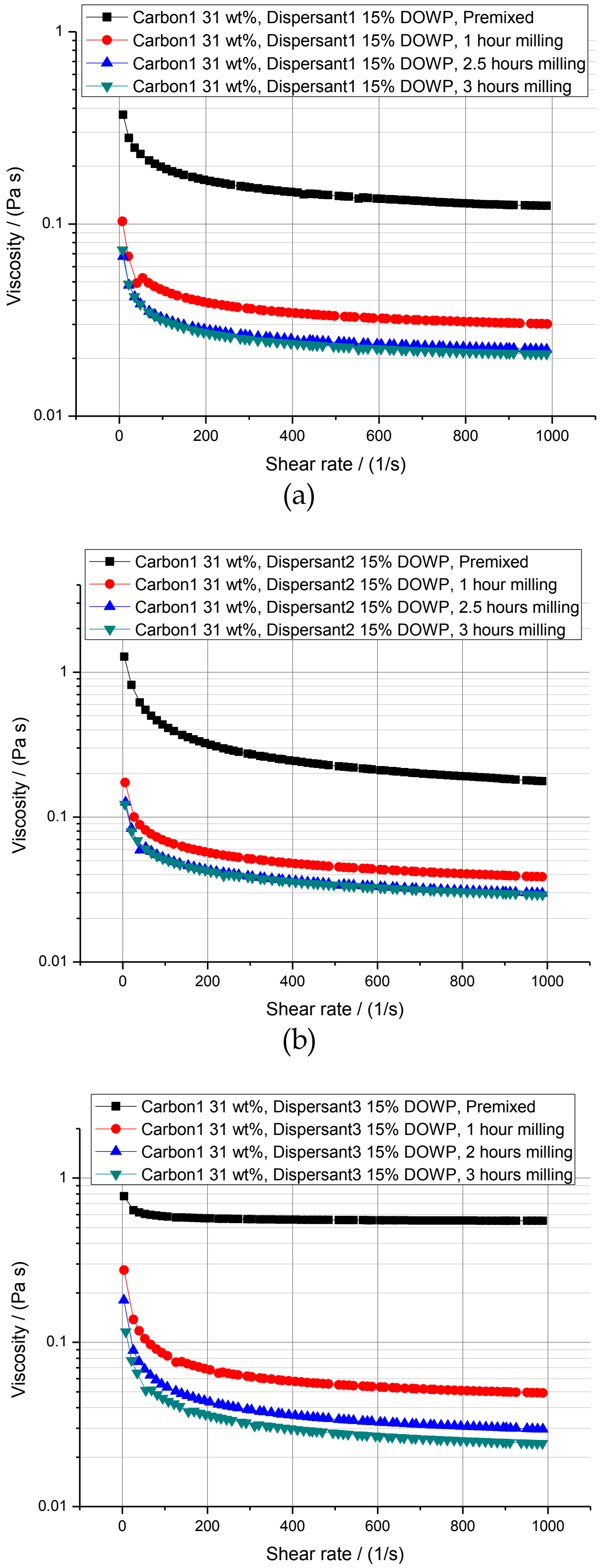
TGA parameter	Description
Heating method	Ramp – Isothermal for 10 minutes at end temperature
Heating rate (^{o}C/min)	10
Start temperature (^{o}C)	25

End temperature (^{o}C)	800 – 825
Test atmosphere	Nitrogen purge

4. Results and Discussion

4.1 Optimum bead milling duration

It is well-known that a decrease in the viscosity of a pigment dispersion can be considered as being a direct indication of the reduction in particle-particle interaction. Since one of the main aims of this study was to optimise the milling of highly viscous dispersions, therefore, the milling effect was analysed at regular intervals during milling by recording the viscosity profiles of all of the pigment-dispersant combinations mentioned in Table 3. It was observed that the most significant reduction in the viscosity of Carbon1 dispersions occurred during the initial one hour of bead milling, as shown in Figure 3. This was followed by only a slight reduction in the viscosity as the milling was continued for another 1 – 1.5 hours. Upon continuing the bead milling for another 30 minutes, a slight decrease in the viscosity of Carbon1-Dispersant3 dispersion was observed, while virtually no change in the viscosity of Carbon1-Dispersant1 and Carbon1-Dispersant2 dispersions was recorded. A more or less similar pattern of reduction in the viscosity was observed for the dispersions of Carbon2, as depicted in Figure 4. The initial 1 hour of milling resulted in the most pronounced reduction in the viscosity of the dispersions. As in case of dispersions of Carbon1, there was very small change or virtually no change in the viscosity of the dispersions of Carbon2 after 2 hours of milling. Therefore, based on the results of the rheological assessments, it was concluded that three hours of milling at 3750 – 4000 RPM effectively dispersed the carbon black pigments despite the considerably different rheological characteristics of their pre-mixed dispersions.

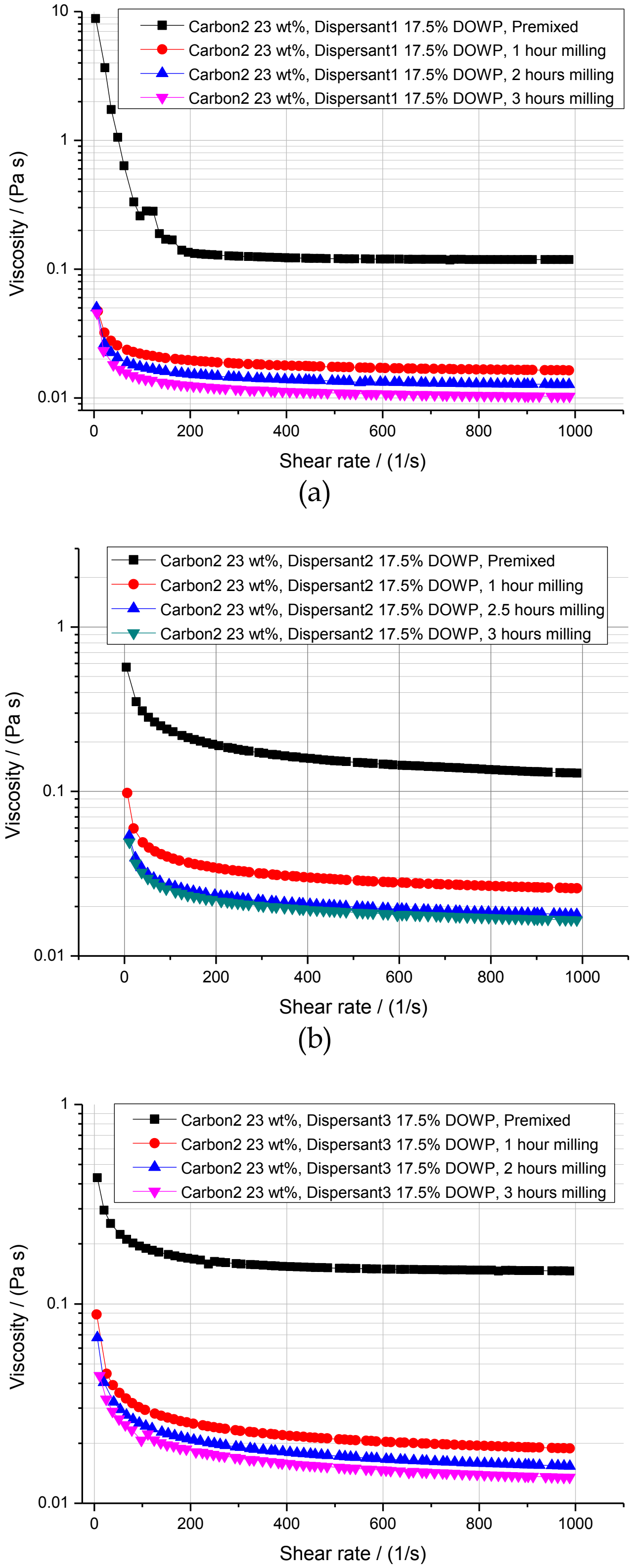


(a)

(b)

(c)

Figure 3: Milling viscosity of dispersions of Carbon1 prepared using (a) Dispersant1, (b) Dispersant2 and (c) Dispersant3.



(a)

(b)

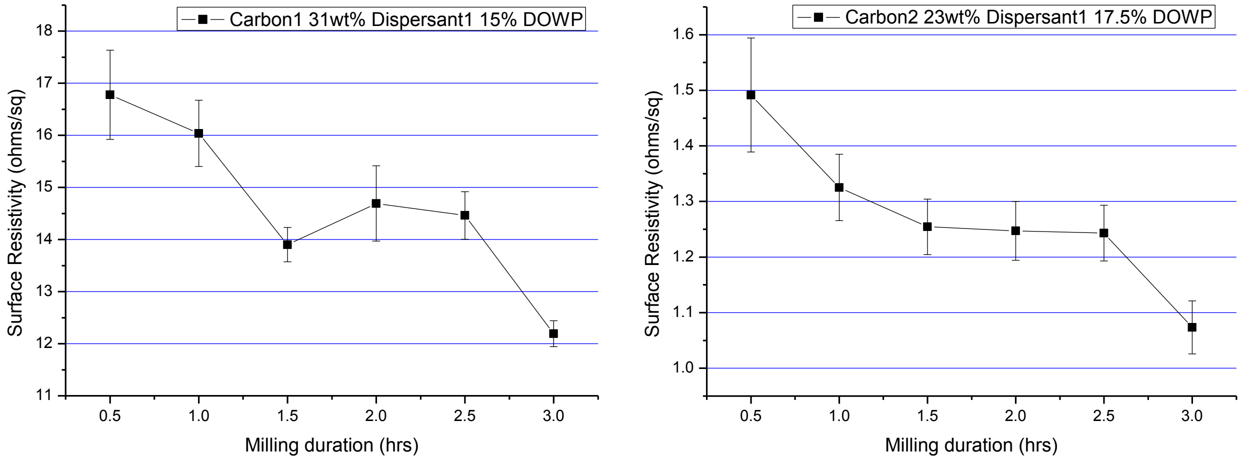
(c)

Figure 4: Milling viscosity of dispersions of Carbon2 prepared using (a) Dispersant1, (b) Dispersant2 and (c) Dispersant3

4.2 Electrical characterisation

In the case of electrically conductive pigments, the electrical characteristics can also be used as an indicator of the state of dispersion of pigment. In this study, the surface resistivity of drawdowns of dispersions was measured to further validate the trends observed in rheological analyses. For this purpose, the dispersion formulations containing Dispersant1 were used. This is because, the viscosity profiles presented in Figure 3 and Figure 4 clearly show that this dispersant was the most effective in reducing the viscosity during milling.

As shown in Figure 5, a gradual decrease in the surface resistivity was observed for the dispersions of both Carbon1 and Carbon2. This trend is in-line with the rheological assessments and it can be regarded as a clear indicator of improved state of dispersion as the milling progressed.



(a) (b)

Figure 5: Surface resistivity of drawdowns of dispersions collected during milling.

4.3 Reliability of the bead milling process

In the context of this study, reliability of the milling process particularly refers to the amount of pigment that was present in different batches of a dispersion after bead milling. For this purpose, two batches of all the pigment-dispersant combinations (Table 3) were prepared and thermogravimetric analysis was done for each milled sample. The thermograms of both batches of a dispersion were compared for similarity in weight loss profile and final pigment loading. The pigment loading, as obtained from the thermogram of the dispersion, was also compared with the pigment loading in starting formulation to estimate the amount of pigment or the amount of water (dispersion medium) lost (if any) during bead milling.

During TGA, the production of carbon char or other decomposition products was possible as a result of the thermal decomposition of the polymeric dispersants present in a dispersion. Therefore, thermal analysis of the as-supplied dispersants was carried out to quantify the amount of residual matter at different temperatures. The thermograms showing the weight loss profiles of the dispersants are provided in Figure 6.

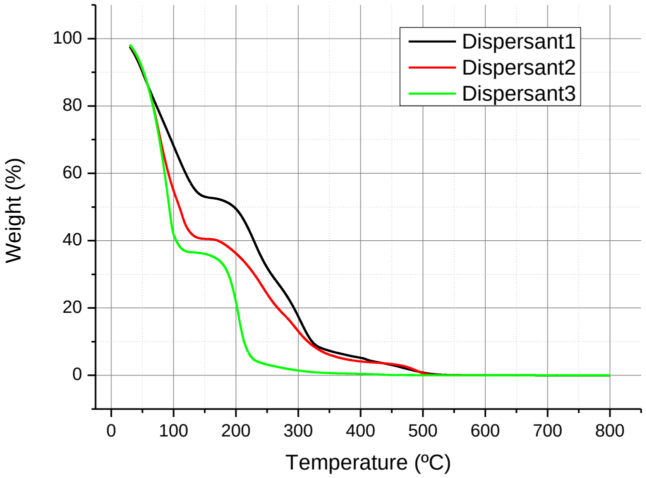


Figure 6: TGA thermograms of Dispersants (as-supplied form).

It is clear from the data presented in Table 5 that a considerable amount of residual matter was not present in any of the dispersants at a temperature of ≥ 600 ºC. On the basis of this information, the thermal analysis of the formulated, bead milled dispersions was carried out at a temperature of up to 825 ºC. Furthermore, the dispersion test specimen was held at 825 ºC for 10 minutes to facilitate complete removal of the decomposition products (if present) of the respective dispersant. It is proposed that the residue from a dispersion sample at 825 ºC, or at a lower temperature at which the respective dispersant was expected to be completely removed, can be regarded as the amount of carbon black pigment in the dispersion recovered from the bead mill.

Table 5: Solids contents of dispersants at various temperatures in TGA.

	Residue (%wt) at different temperatures				
	400 ºC	**500 ºC**	**600 ºC**	**700 ºC**	**800 ºC**
Dispersant1	5.20	0.82	0.03	0.01	0.00
Dispersant2	4.13	0.63	0.04	NA*	NA*
Dispersant3	0.45	0.06	0.05	0.03	0.02
*NA refers to ‘solids content not measureable’					

The thermogravimetric analyses showed that the weight loss profiles of the different batches of Carbon1 pigment dispersions were very similar, as shown in Figure 7. The solids content in the different batches of the dispersions of Carbon1 pigment are tabulated in Table 6. It was found that the pigment loading in both batches of Carbon1-Dispersant1 dispersion was similar, though it was above 34 wt% which is higher compared to that in the starting formulation. In contrast, in the dispersions of Carbon1 pigment that were prepared using Dispersant2 and Dispersant3, the amount of pigment was close to that in the starting formulations, which was 31 wt%. The TGA analyses showed that, with the exception of Batch 1 of Carbon2-Dispersant3 dispersion, the amount of pigment in the bead milled dispersions of Carbon2 was in the range of 24 – 27 wt% which is greater than the pigment loading of 23 wt% in the starting formulation. It was observed, as shown in Figure 8(c), that the weight loss continued in Batch 1 of the Carbon2-Dispersant3 dispersion when the sample was heated above 500 °C and that the solids content at 825 °C was 19.80 wt%. However, the TGA data of this dispersion showed that the solids content at 500°C was approximately 25 wt%. Since the TGA showed that the amount of residue of Dispersant3 was 0.06% at 500 °C, the decrease in solids content above 500 °C could not be regarded as a direct indicator of lower pigment loading in this dispersion formulation.

Table 6: Pigment loading as obtained from the formulation calculations and TGA of the bead milled dispersions.

Dispersion name	**Pigment loading (wt%)**		
	Starting formulation	**TGA of bead milled dispersion***	
		Batch 1	**Batch 2**
Carbon1-Dispersant1	31	35.16	34.24
Carbon1-Dispersant2	31	31.81	30.97
Carbon1-Dispersant3	31	31.74	31.29
Carbon2-Dispersant1	23	26.27	26.59
Carbon2-Dispersant2	23	26.99	24.97
Carbon2-Dispersant3	23	19.80	24.30
* Solids content at 825 °C			

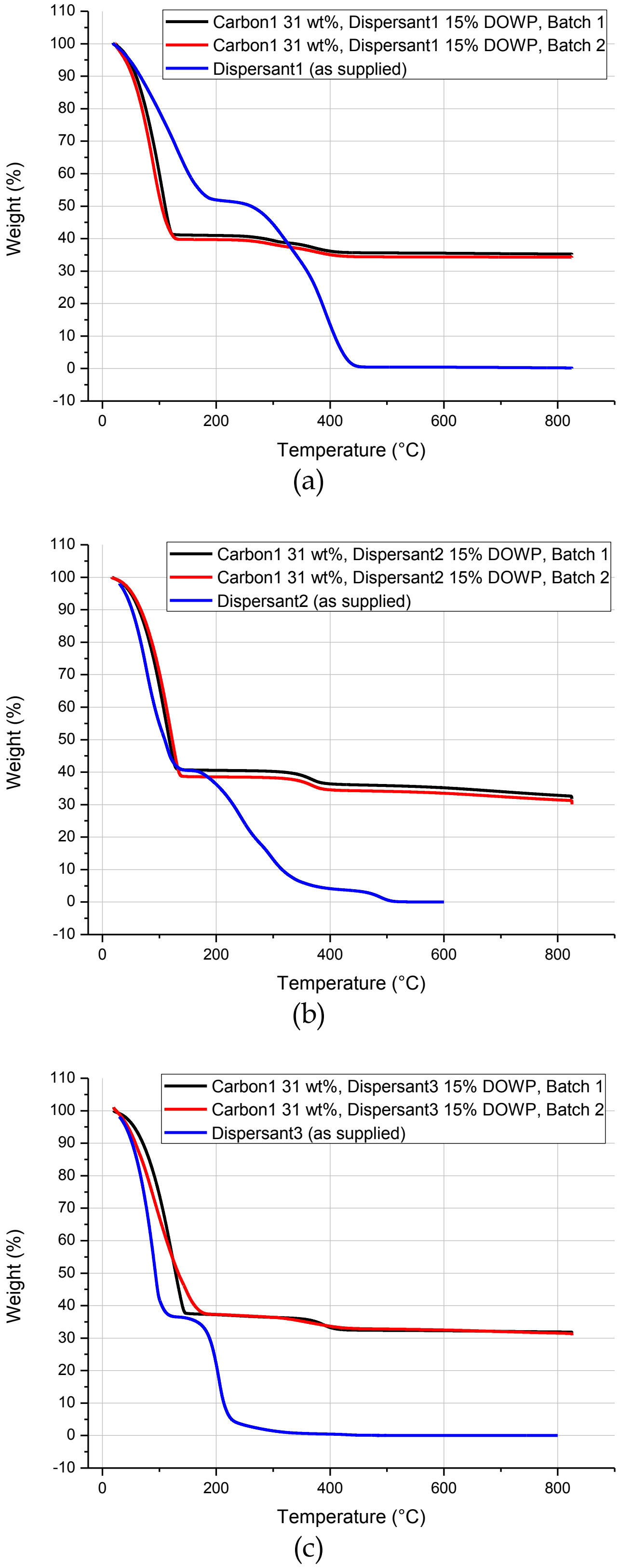


Figure 7: TGA thermograms of different batches of dispersions of Carbon1 prepared using (a) Dispersant1, (b) Dispersant2 and (c) Dispersant3.

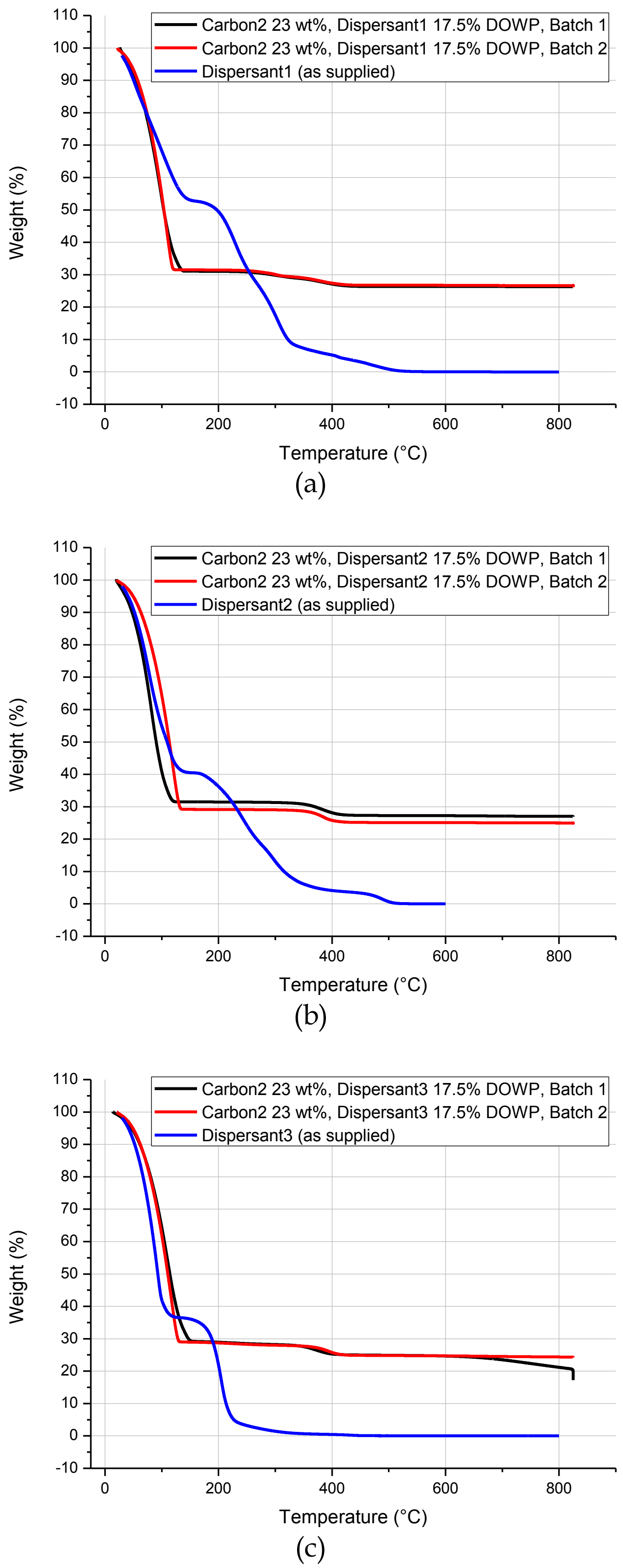


Figure 8: TGA thermograms of different batches of dispersions of Carbon2 prepared using (a) Dispersant1, (b) Dispersant2 and (c) Dispersant3.

The batch-to-batch variation in terms of the pigment loading in the bead milled dispersions was generally very limited. However, it was also clearly observed that the pigment loading in bead milled dispersions was different than that in the starting formulations. This can be attributed to the fact that the bead mill used in this work was not a closed system and during three hours of milling operation, some water loss was likely to occur. Water loss was also facilitated by the slight increase of temperature that was observed during initial several minutes of milling of the high viscosity pre-mixed dispersions.

5. Conclusions

In this work, it is shown that a laboratory bead mill that is designed primarily for low viscosity dispersions can be used for milling of high viscosity dispersions of pigments that are difficult to disperse (e.g., dispersions of carbon black pigment). We have devised a method to establish the optimum milling parameters for a particular type of pigment-dispersion system. In addition, a method is proposed to ascertain the repeatability of milling operation by recording the thermograms of multiple batches of a dispersion formulation. In this study, waterborne dispersions of carbon black pigments were prepared and characterised. However, based on the fact that the selected pigment grades contained very low volatile matter content and were dispersed in water (a polar medium), it is proposed that same method(s) can be applied to other demanding dispersions. By such an approach, it can be ensured that pigment dispersions possessing a range of viscosities are bead milled effectively. Our study suggests that pigment loss or changes in formulation composition such as the amount of solvent can occur during milling operation. Therefore, it is important to determine the pigment loading after milling in order to avoid any unexpected trends in the final product characteristics.

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