THE HIGH CONCENTRATION COLORED MASTERBATCH: INFLUENCE OF PARAFFIN WAX AND PREMIXING PROCESSING METHOD ON DISPERSION QUALITY

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ABSTRACT

Among major problems encountered by manufacturers of highly concentrated color masterbatch is the poor dispersion of the pigment caused by the strong tendency to build up agglomerations of powdered pigment particles. The aim of this study is to characterize the effect of the conditions of the premixing process and the formulation of the master batch of high concentration 40% on the quality of the dispersion. We studied the influence of the speed, temperature, time and order of the introduction of the premix ingredients and the use of a wetting agent on the dispersion quality by the colouring strength measurement and pressure test by filtration. A study by optical microscopy was considered.

Key words: Masterbatches, Processing parameters, Thermoplastics matrix, Coloration process, Premixing, Dispersion quality, Wax.


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1. INTRODUCTION

Masterbatches are widely used in the plastics industry to add color and other desired properties to products [1, 3]. Thanks to constant technological development, more efficient processing plants, new fields of application, cost savings…, there is a daily demand for new solutions and more efficient and sophisticated products. Only the objectives of masterbatches producers remain the same: a higher concentration of pigment at the same time as a higher dispersion quality. Plastic thin products such as strips, rope and filaments, which require the use of high-concentration masterbatch for to be tinting, are most concerned with the degree of
pigments dispersion or additives. Dispersion problems arise when the aggregate particles interact to produce agglomerates [2]. Improved wettability of the particles with complete aggregate destruction leads to good particle dispersion and this is demonstrated by the constancy of the number of particles as a function of time [4]. The problem that remains is the natural tendency of particles to reduce their number over time because of the coalescence phenomena, linked to the attractive forces that exist between the particles [5, 6]. The magnitude of the coalescence phenomena depends on the pigment concentration volume, the particles physical properties, the environment viscosity and temperature. The stability of pigment dispersion depends on the free energy of overall interaction between the two dispersed pigment particles. The global interaction free energy is a combination of Van der Waals interactions, electrostatic interactions and steric interactions [7, 8]. However, difficulties in pigment dispersion can be overcome by particularly reducing the viscosity of the mixture [9, 10].

More the size of the pigment particle is smaller, more complete the capacities and inherent properties of the particle will be and the better the results are expected [11]. In many cases, the base polymer in granules form alone is not sufficient to achieve the required dispersibility and hence wetting agents and / or dispersants become necessary. Wetting and dispersing agents are very effective and provide an easy way of making masterbatches with good pigment dispersion.

The quality of the final dispersion depends on the optimization of many factors. In a previous study [12], we showed that the screw configuration design and the temperature profile strongly influenced the dispersion process. Another study is interested in manufacturing a mono concentrated purple masterbatch based on dioxa zinc pigment, showed that a better combination of processing parameters by the extrusion process to optimize pigment dispersion and reduce clogging power.

The mixing process from three extrusions without filtration leads to a reduction in the filter pressure value (FPV) of about 84% and an increase in the relative colouring strength (RCS) of about 50% Compared to the standard production process (a single extrusion) for the manufacture of a polyamide 6 monodispersed green masterbatch with a halogenated copper phthalocyanine green pigment [14].

The modification of masterbatches formulation by the addition of waxes and / or powders of micronized polyolefin make it possible to improve the quality of dispersion. Arno Knebelkamp [15] has shown that using powders of micronized polyolefin obtained by cryogenic grinding or with an air jet mill in the pigment concentrates formulation for coloring plastics improves the pigment dispersion quality.

Andreas Seidel [16] proposed a method for improving the carbon black dispersion using a wetting agent comprising low molecular weight wax, lignite and aliphatic or aromatic wax oils, carboxylic acid esters, fatty acids and / or fatty alcohols. It has also shown that the impact strength of notched specimen is significantly higher and the number of surface defects is reduced compared to carbon black used alone.

The masterbatches manufacturing is a two-stage process: collecting ingredients and mixing them, then processing them together by applying heat and shear to produce homogenized granules. In general, variable speed mixers are used to produce a premix which is then processed in twin screw extruders. This treatment depends on several key elements: the formulation, the raw materials quality, and the mixture quality [17, 18].

A number of factors affect the product final quality relative to the dispersion level obtained during the mixing process. Mixing time, blade speed, mixing temperature and the
order in which the ingredients are introduced are just a few of the factors influencing dispersion [19, 20, 21]. The effect of these factors is often difficult to determine because of the strong interactions between them [3].

The aim of this study is to determine a precise way the impact of the different mixer parameters on the masterbatch dispersion level. We studied the speed, the time, the temperature and the ingredients introduction order on the dispersion quality. We also studied the effect of using paraffin wax as a wetting agent in the masterbatch formulation as well as its percentage on the dispersion degree.

2. EXPERIMENTAL PROCEDURE

2.1 Materials

The base polymer selected for this study was a polypropylene homopolymer PP GRAIN511A issued by Sabic Belgium with an MFI of 25 g / 10 min (230 °C and 2.16 kg), a melting temperature of 155 °C. The type of the red pigment used is PR 48: 3, sold by Hangzhou AiBaiChemicalCo., Ltd. It is presented in powder form, density = 1.8, oil intake (ml / 100g)% between 45-55, and light resistance= 8. The Licocene PP 1502 wax and Licocene PP6102 wax softening temperatures are 86 °C and 145°C respectively, provided by Clariant. These waxes have been used as wetting agents to positively influence the dispersion degree.

Two formulas have been developed which are presented in Table 1. The presence of waxes in the formulations is absolutely necessary in order to guarantee effective pigments wettability and to limit the particles agglomerations constitution.

Table 1: Formulation details

<table>
<thead>
<tr>
<th>S. N°</th>
<th>Ingredient</th>
<th>Formulation 1 % w/w</th>
<th>Formulation 2 % w/w</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PP GRAIN511A</td>
<td>22.5</td>
<td>22.5</td>
</tr>
<tr>
<td>2</td>
<td>Antioxidant B225</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>3</td>
<td>PP poudre</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>4</td>
<td>Cire Licocene PP 6102</td>
<td>0</td>
<td>20</td>
</tr>
<tr>
<td>5</td>
<td>CireLicocenePP 1502</td>
<td>20</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>Calcium Stearate</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>7</td>
<td>PR 48: 3</td>
<td>40</td>
<td>40</td>
</tr>
<tr>
<td>8</td>
<td>Plastaid – T</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

A double screw extruder type Nanjing Hisilicon Extrusion Equipment Co., Ltd. TSE40 with the following characteristics: L / D = 40, specific torque = 8.2 Nm / cm3 (30 kW at 600 rpm) and capable of operating at 600 rpm. The screw speed was set to 200 rpm. The different formulations were premixed by a mixer type (power 58kw) capable of rotating up to 1000 rpm. The mixer speed was set at 100 rpm, 350 rpm, 500 rpm and 500 rpm and the mixing time varied between 3 to 20 min.
2.2 Filter test and relative coloring strength
Two characterization techniques of dispersion degree were developed in a previous study [12], the filter pressure value (FPV) and an increase in relative colouring strength (RCS) were used to evaluate the dispersion quality.

2.3 Reflection optical microscopy
To establish the relationships between the different parameters of the pre-mixing process and addition of waxes on the one hand, and the dispersion degree on the other hand, we carried out a series of observations under the reflective optical microscope, in order to characterize the dispersion quality of our highly concentrated masterbatches.

3. RESULTS AND DISCUSSION

3.1 The dispersing agent: Type choice effect
A masterbatch is composed of a polymeric matrix in which a varied proportion (5-80%) of pigments and / or colorants, dispersing waxes and other additives are included. The use of special waxes - in particular high-quality wetting agents - and their optimum adaptation to the pigments requirements, carrier systems and relevant processing technology enable efficient and consequent realization. The choice of the wax type used appears necessary to achieve the objectives. We have studied two waxes: PP LICOCENE 1502 and PP LICOCENE 6102. They are used at 50% relative to the pigment percentage. The various formulas are introduced into the mixer container in the order given in Table 1. The patch weight is 40kg. Both of two formulas are mixed for 10 minutes with a rotating helix at a rate of 300 rpm. We have taken as reference the formula without dispersing agent at a speed of 300 rpm.

![Figure 1](http://www.iaeme.com/IJARET/index.asp) 4  
**Figure 1** The coloring strength evolution as a function of the wax type
Figures 1 and 2 represent successively the variation of the coloring strength and the pressure by filtration as a function of the wax type chosen. The waxes stabilize the dispersion and prevent any fine particles of pigment, formed during the dispersion process, from reagglomerating as well as avoiding local overconcentration. The results clearly show that the wetting agent type choice has a significant impact on the evolution of the coloring force and the pressure, the wax which has a higher melt index shows better results.

Dispersion is the complete wetting of the pigment agglomerates - not only on the agglomerate surface but also on all the particles surfaces, both inside and outside [22]. Only using special waxes allows the pigments optimum wetting, so that even the hollow and fine spaces between the agglomerated particles become accessible to the wetting agent.

It is evident that a low viscosity wax may have advantages in this regard compared to a higher viscosity wax. The pigment polarity, its particle shape, its size and its surface are important factors in the selection and dosage of a suitable adjuvant, as well as its thermal and mechanical properties [11, 22].

Due to the low viscosity, reduced by adding wax, longitudinal and lateral intensive mixing in the double extrusion machine becomes easier. Even this aspect is of great importance, since excellent mixing is among the prerequisites for effective wetting, dispensing and homogenization of pigments and additive particles.

3.2 Concentration effect of dispersing agent

The wetting efficiency depends mainly on the pigment surface tension properties and the base polymer, as well as the resulting mixture viscosity [24]. The absorption mechanism depends on the pigment chemical nature and the type and volume of wetting agents used. The viscosity plays an important role on the one hand, the use of a certain amount of wax is recommended to improve substantially the wetting and pigments distribution. On the other hand, this measurement results in a viscosity reduction of the concentrate melt and makes it possible to increase the pigments concentration.

According to the pigment type, the optimum dispersion requires up to 40% of wax relative to the pigment weight [91]. Excessive wax amounts always result in migration and deposition on the matrices [23], it is particularly advantageous in the pigment concentrate preparation containing well-dispersed pigments with minimum fractions of polyolefin waxes.
Figures 3 and 4 show the coloring strength evolution and the pressure evolution for different levels of dispersing agent relative to the pigment weight. These same figures show that the increase in waxes volume fraction increase very substantially the coloring strength and decreases the pressure and consequently increases the masterbatch dispersion degree. The wax percentage must be sufficient to avoid the pigment's particle agglomeration and ensure good wetting of these particles in the mixture. We have found that the optimum dispersion requires up to 35% by the pigment weight. Increasing the wax content to values above 35% does not always produce good results. Reducing the viscosity at certain values reduces the shear effect generated by the screws during the extrusion step. The aim of this work is to prepare pigment concentrates having the lowest possible level of polyolefin waxes and at the same time a good dispersion quality.
3.3 Mixer parameters effect

A series of experiments have been conducted to assess the importance of premixing conditions of masterbatches, study the influence of the mixer blade speed, after the ingredients have been introduced into the container, batches of 40 kg were mixed at 200 rpm, 300 rpm 400 rpm 500 rpm and 600 rpm for 5, 10 and 15 minutes. In addition we measured the temperature of each prepared sample. Figure 5 shows the premixing conditions effect on masterbatches dispersion quality.

![Figure 5](image)

**Figure 5** The coloring strength evolution as a function of time and of mixing speed

![Figure 6](image)

**Figure 6** The mixture temperature evolution as a function of time and of mixing speed.

The dispersion results obtained (Figure 5) and the monitoring of the mixture temperature change (Figure 6) have shown that the parameter most relevant for the dispersion quality is the mixture temperature. A higher temperature level has considerably improved the dispersion degree. We have found that the higher the temperature, the more dust-free, free-flowing powder mixture is obtained. This can also offer the advantage of facilitating the masterbatches...
extrusion. In order to reach temperatures close to the wax softening point. We changed the ingredients introduction order, in the first time we mixed PP grain, PP powder, antioxidant, calcium Stearate and wax at a speed of 600rpm for 20min. The temperature obtained is 90 °C., after adding the pigment and Plastaid-T also mixed at a speed of 600 rpm for 15 min to reach a temperature of 80 °C. When this temperature level is exceeded, the mixture presents difficulties during extrusion. The figure. 7 shows the dispersion quality evolution obtained by the new procedure. We noted a 56% increase in coloring strength when the pouch temperature of the wax softening point is increased by heating the mixture. The pigment is moistened with the wax, which makes the mixture virtually dust-free. In addition the pigment-wax mixture forms a thin skin around the polymer granule, so that the wax functions as a binder. This coating acts as a distance guard between the pigment particles. The wax particles in the pigment particles vicinity and being substantially distributed have a high probability of finding a place between the pigment particles, thus separating them from one another. Consequently, these pigment particles will not form an agglomerate, which facilitates pigments dispersion and finally stabilizes it.

Figure 7  The coloring strength evolution as a function of the new premixing procedure

The remarkable increase in the coloring strength allows a possible reduction in the amount of pigment and wax. It is a way to have economic formulation costs and good performance without treatment problems. The reduction of the wax content also makes it possible to reduce the effect of migration on the granules surface which can affect the product quality during its storage.

3.4 Microscopic analysis

In order to validate the results obtained previously on the interaction between the conditions of the pre-mixing process and the formulation of the masterbatch on the one hand and the dispersion quality on the other hand. We carried out a series of morphological analysis using optical microscopy according to the parameters used.

Figure 8 shows the variation in the dispersion degree by a standard film with different parameters studied. A better dispersion is presented for the new procedure used (FIG. 8F), we have found that the agglomerates are almost disappeared and the film is characterized by a more reddish contrast marking the increase in the coloring strength and consequently a better dispersion. This corresponds to the results obtained above.
Figure 8 Microscopic visualization of masterbatches with different mixture parameters

(A) Without wax, (B) with Licocene wax PP 6102, (C) with Licocene wax PP 1503 (D) Speed 300 rpm and time 10 min, (E) speed 600 rpm and time 20 min, (F) With the new protocol,

4. CONCLUSION
Dispersion is an inherent property of the pigment and the process used to produce the masterbatch. Good dispersion is particularly required when the final application requires well-required performance. A better understanding of the conditions effect of the mixtures preparation before their treatment by extrusion is critical for better dispersion. This study allowed us to show the formulation effect and the pre-mixing conditions on the dispersion
level. The choice of the type and the rate wax used appear necessary. Using 17.5% of the Licocene PP1502 wax considerably improves the dispersion degree. The application of a new procedure, by increasing the mixture temperature to 90 °C., makes it possible to increase the colouring strength by 56% by improving the mixture quality, powdered and dust-free, the wax acts as a binder and fixes the pigments particles on the polymer surface which facilitates the dispersion. These results are validated by microscopic analyzes.

REFERENCES


