

## Coloration Properties and Chemo-Rheological Characterization of a Dioxazine Pigment-Based Monodispersed Masterbatch

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**ABSTRACT:** A dioxazine-based color pigment was added to a commercial polyamide 6 (PA6) through an extrusion process, in order to prepare monoconcentrated violet masterbatches through different production set-up. A detailed characterization of the resulting materials was carried out in order to find the best processing parameters combination to optimize pigment dispersion and to reduce the clogging power. The preparation of masterbatches with repeated extrusions markedly reduced the filter pressure value and increased the Relative Color Strength, while filtration did not significantly influence pigment dispersion. Rheological measurements and end-groups analysis were conducted on the same materials with the aim to evaluate their thermal degradation resistance, and the thermal stability of the compounds was retained even upon three extrusions. Therefore, it can be concluded that a proper optimization of the process parameters could lead to an important reduction of the production waste, increasing the quality of the final product. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41452.

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### INTRODUCTION

Since prehistory coloration technology has always played an important role in development of the human society, especially from an anthropological, aesthetic, functional and economic point of view.<sup>1,2</sup> Also plastic materials market is strongly connected to the coloration industry, because of the growing need of innovative color masterbatches with elevated physical and chemical performances. From an industrial point of view, plastic materials coloration can be performed in two ways: by using soluble dyes or color pigments.<sup>3</sup> Soluble dyes are organic compounds that can be solubilized with the plastic substrate. The transparency of the compounded materials can be usually retained, thanks to their good chemical affinity with the greatest part of polymer matrices. Color pigments are constituted by very fine and insoluble particles that can retain their pristine properties both during the manufacturing and during the service life of the plastic product.<sup>3</sup> Physically speaking, pigments impart color to the plastic medium by a selective light absorption in the visible spectrum.<sup>1</sup> Color pigments must satisfy some important technical requirements: (i) easy dispersion within the matrix, (ii) chemical stability even under heavy thermo-mechanical processing conditions, (iii) compatibility with the other additives, (iv) total insolubility in the host matrix, (v) non-toxicity, and (vi) environmental compatibility.<sup>4,5</sup> Except for

titanium dioxide (TiO<sub>2</sub>), inorganic pigments generally possess elevated light absorption capability and low scattering properties. They are characterized by elevated stability at high temperatures (up to 300°C), but they have a lower color strength in comparison to organic pigments. Because their elevated surface energy promotes primary particles wettability and reduces filler agglomeration, inorganic pigments can be easily dispersed in polymers even at low shear stresses.<sup>5</sup> The most important inorganic pigments in the plastic industry are CI Pigment White 6 (TiO<sub>2</sub>) and CI Pigment Black 7 (Carbon Black). On the other hand, organic pigments are polycyclic molecules containing chromophoric groups. Considering that they are generally insoluble with the greatest part of polymer matrices, they show a lower dispersability with respect to organic pigments, especially in polyolefins, and their heat resistance is often limited to 280°C.<sup>5</sup> In the open literature it was reported how organic pigments are able to play a marked nucleating activity on polymer matrices, increasing crystallization kinetics.<sup>6</sup> Blue and green copper phthalocyanine (CI Pigment Blue 15:3 and CI Pigment Green 7) and violet dioxazine (CI pigment violet 23) are probably the most important organic pigments.<sup>5</sup>

In the greatest part of the industrial coloration processes, color pigments are not used in powder form, but they must be compounded with polymers for the production of

monoconcentrated masterbatches in filler concentrations ranging from 5 to 40 wt %. These concentrates are then added to the neat polymers through an extrusion process in a mass coloration process.<sup>4,5</sup> Compared to color powders, monodispersed masterbatches are more safe (i.e. avoidance of dust in the working place) and are preferable in terms of product quality (i.e. better pigments dispersion, higher color strength, reduced cleaning time).<sup>3</sup> Mass coloration can be generally carried out starting from the preparation of the monodispersed masterbatch, that could be subsequently added to the polymer matrix.<sup>5</sup> Monoconcentrated masterbatches can be prepared through an extrusion process by mixing together powder and polymer matrix. Elevated shear stress during the extrusion promotes the breakage of primary particles aggregates and improve polymer-particles wettability. This process can be favored applying elevated processing temperatures and by using a low viscosity matrix.<sup>7,8</sup> Pigment dispersion in the polymer matrix and their agglomeration propensity depend on the properties of the filler (i.e. size, shape, surface properties, crystalline structure, chemical composition of the primary crystals).<sup>4</sup> On the other hand, filler aggregation may cause heavy technical limitations like embrittlement, breakage during spinning, low coloration quality and the increase of the production times and scraps.<sup>4</sup> Amorphous particles generally have higher surface energy compared to crystalline particles, and therefore they are characterized by a marked tendency to agglomerate or to absorb other chemical species (i.e. solvents or surfactants).<sup>1</sup> According to the works of Deshmukh et al.<sup>3</sup> and Ahmed et al.,<sup>4</sup> the most difficult pigments to disperse are CI Pigment Blue 15:3, CI Pigment Green 7 and CI Pigment Violet 23.

The evaluation of the pigment dispersion within the matrix has a key role for the color masterbatch quality assessment. Direct investigation techniques, such as microscopical analysis and X-ray fluorescence (EDX), can be considered, while indirect methods such as Filter-Test, Color Strength and rheological measurements<sup>4</sup> are more representative, because they are strictly connected to the production process and to the optical properties of the yarns.<sup>5</sup> According to our knowledge, only few articles focused on the analysis of monodispersed masterbatch production process and to the optimization of pigments dispersion in polymer matrices can be found in the open literature. For instance, Joshi et al. evaluated the effect of surfactant agent on the particles dispersion by measuring torque variation in the extruder during the melt compounding.<sup>7</sup> Suresh et al. investigated pigments dispersion in a low density polyethylene matrix comparing different kinds of monodispersed masterbatches.<sup>3</sup> Ahmed et al.<sup>4</sup> compared the mechanical properties of polypropylene fibers obtained by using pigments in powder form and monodispersed masterbatches. Wo et al. studied the effect of phthalocyanine pigments on the crystallization behavior of polypropylene.<sup>6</sup> Moreover, a detailed study of the pigments and their effects on the fibers produced through a spinning process was carried out by Marcincin.<sup>5</sup>

On the basis of these considerations, in this work the influence of different production processes on the pigment dispersion in polyamide 6 (PA6) monoconcentrated masterbatches filled with dioxazine particles was evaluated, with the aim to improve the

**Table I.** Properties of PA6 and Dioxazine Violet Pigment (PV23)

Property	AQ 24000	PV23
Molecule	Polyamide 6	Dioxazine
CAS number	25038-54-4	6358-30-1
Chemical formula	$[C_6H_{11}NO]_n$	$C_{34}H_{22}Cl_2N_4O_2$
Density ( $g\ cm^{-3}$ )	1.14	1.46
$M_w$ ( $g\ mol^{-1}$ )	-	589.48
$\eta_{rel}^a$	2.4	-
$T_m$ ( $^{\circ}C$ )	222	-
BET SSA ( $m^2\ g^{-1}$ ) <sup>b</sup>	-	57.8

<sup>a</sup> Measured through a Ubbelohde viscometer at 25°C on sulfuric acid solutions (concentration = 10 g L<sup>-1</sup>).

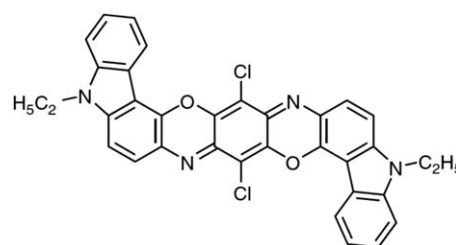
<sup>b</sup> Measured through a ASAP<sup>®</sup> 2010 Accelerated Surface Area and Porosimetry machine.

color strength of master and to limit the clogging effect and the pigments consumption during the spinning process. Therefore, a detailed analysis of the filterability and of the chemorheological behavior of monoconcentrated masterbatches was conducted. This work represents the preliminary step of a wider research project aiming at the investigation of the properties of complex color masterbatches, prepared with different monodispersed compounds.

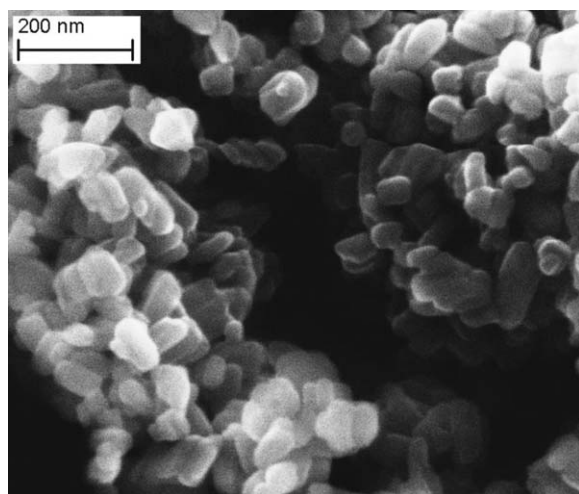
## EXPERIMENTAL

### Materials

An Aquamid<sup>®</sup> AQ24000 PA6 resin with a relative viscosity of 2.4 was kindly supplied by Aquafil S.p.A (Arco, Italy) in form of polymeric chips. A dioxazine violet color pigment powder (CI PV23) was provided by BASF (Ludwigshafen, Germany). The most important physical properties of the PA6 matrix and of the color pigment are summarized in Table I. The chemical structure of dioxazine Violet is represented in Figure 1, while in Figure 2 a representative SEM micrograph of these pigments is reported. It can be easily detected the aggregated morphology of this filler, with the presence of agglomerated primary particles with an irregular shape, having a mean size of 70 nm. The surface properties, the density of the pigments and the theoretical dimension of primary particles were determined through BET analysis and helium pycnometry. Moreover, through light scattering measurements the mean dimension of the agglomerates and the number of primary particles within the aggregates was estimated. The most important results are summarized in Table II.



**Figure 1.** Chemical structure of dioxazine violet (PV23).



**Figure 2.** SEM micrograph of dioxazine violet pigments.

### Monoconcentrated Masterbatches Preparation

Violet monodispersed masterbatch was prepared through a traditional melt compounding and extrusion process. Aquamid 24000 was powdered and mixed with halogenated copper phthalocyanine pigments by using a turbo mixer keeping a constant filler concentration of 25 wt %. The mixture was then extruded in a co-rotating twin screw extruder, having a screw diameter of 58 mm and a L/D ratio of 44. The following process parameters were utilized: rotational speed = 350 rpm, feed rate = 210 kg h<sup>-1</sup>, barrel temperature profile = 80/230/245/245/245/245/250/260°C. After being extruded, the compounded materials passed through an industrial filter with a size of 60 μm, in order to remove the impurities and bigger agglomerates that could potentially clog the filters and lead to the filament rupture during the subsequent fiber spinning. In order to optimize the dispersion quality of the final products, four process set-up, differing for the extrusion number and for the presence of the final filtration, were considered. Physically speaking, an increase of the extrusion times could promote better pigments dispersion, because of the higher dispersion energy applied to the system. Therefore, the different production processes were evaluated in term of Specific Mechanical Energy (SME), evaluated as reported in eq. (1):

$$\text{SME} = \frac{n \cdot P \cdot O}{n_m \cdot Q} [\text{kWh kg}^{-1}] \quad (1)$$

where  $n$  is the screw speed,  $n_m$  is the maximum screw rotations,  $P$  is the electric power,  $O$  is the engine loading, and  $Q$  is the extruder capacity. SME measures energy transfer from drive motor to the heating system for melting, mixing and die pressurization in the compounding process.<sup>9</sup> It gives an evaluation

**Table III.** Production Process Set-up

Production process	Number of extrusions	Presence of filtration process	SME (kWh kg <sup>-1</sup> )
1 Extrusion W-F	1	Yes	0.247
1 Extrusion W/O-F	1	No	0.229
2 Extrusions W/O-F	2	No	0.458
3 Extrusions W/O-F	3	No	0.688

of the energy consumption during the extrusion and provides some information about extruder efficiency.<sup>10–15</sup> On the other hand, it is well known that a prolonged thermal treatment (i.e. elevated SME values) could lead to a serious degradation of the polymer matrix. In Table III the most important parameters of the different processing conditions with the relative SME values are summarized. The compounded materials were then pelletized and injection moulded through a Battenfield Plus 350/075 machine, in order to prepare square sheets 2 mm thick suitable for color strength measurements.

### Experimental Methodologies

**Filter Pressure Value Analysis.** The dispersion of the filler within the polymer matrix is directly correlated to the industrial filterability of monoconcentrated masterbatches, and it was evaluated through Filter-Test measurement, performed according to EN 13900-5 standard.<sup>16,17</sup> Monoconcentrated masterbatches were processed through an extruder (L = 33.6 cm, L/D = 24, rotational speed = 20 rpm, barrel temperature profile = 270/270/270/275°C), and the molten polymer passed through a filter with a size of 25 μm. The pressure increment due to the filter clogging was measured.<sup>3,5</sup> Filter-tests give the so called filter pressure value (FPV) and plateau filter pressure value (FPVII), defined as reported in eqs. (2) and (3):

$$\text{FPV} = \frac{P_2 - P_1}{M} \quad (2)$$

$$\text{FPVII} = \frac{P_3 - P_1}{M} \quad (3)$$

where  $P_1$  is the initial pressure,  $P_2$  is the maximum pressure,  $P_3$  is the second pressure plateau after pressure peak, and  $M$  is the mass of pigment passed through the filter. A low FPV value means that the extrusion process led to an homogeneous dispersion of the pigments in the matrix, while elevated FPV indicate a bad filler dispersion within PA6. Industrially speaking, FPV gives a quantitative evaluation of the masterbatch processability and of its suitability for the spinning process, while FPVII provides information about filter clogging phenomenon. In particular, a slight pressure drop after the pressure peak can

**Table II.** Experimental Results of BET, Light Scattering, and Density Measurements on Dioxazine Pigment

Pigment	Density <sup>a</sup> (g/cm <sup>3</sup> )	SSA <sup>b</sup> (m <sup>2</sup> /g)	d <sub>BET</sub> (nm)	d <sub>Light scattering</sub> <sup>c</sup> (nm)	N primary particles
Violet PV23	1.47	57.11	72	187	3

<sup>a</sup> Measured through a Micromeritics® Accupyc 1330 helium pycnometer.

<sup>b</sup> Measured through an ASAP® 2010 Accelerated Surface Area and Porosimetry machine.

<sup>c</sup> Measured through a Beckman Coulter-Desla® Nano C-Particle analyzer.

be related to a physical clogging of the filter, due to the packing effect of the aggregates, while a marked pressure decrease may be due to the presence of unstable agglomerates or gels that were broken down and pushed through filter from the flow of the molten polymer.

### Color Strength

The color strength identifies the property of a pigment to impart color to a substrate under specific processing conditions.<sup>18,19</sup> The reflectance curves of samples were determined through a Hunterlab<sup>®</sup> Colorquest XE Spectrophotometer. According to the two-flux radiation theory of Kubelka–Munk (KM),<sup>20</sup> the measured reflectance of an optically infinite thick layer  $R_{\infty}(\lambda)$  is related to the ratio of the absorption coefficient  $K(\lambda)$  and the scattering coefficient  $S(\lambda)$  for diffuse light, as reported in eq. (4):

$$\frac{K(\lambda)}{S(\lambda)} = \frac{[1 - R_{\infty}(\lambda)]^2}{2 \cdot R_{\infty}(\lambda)} \quad (4)$$

From eq. (4) the absorption coefficient  $K(\lambda)$  over the whole interval of visible light was calculated and weighted with the tristimulus curves, and the pigment amount necessary to obtain the same reference color intensity was computed. The Relative Color Strength (RCS) was determined comparing the (K/S) ratio of the sample with that of a standard reference,<sup>16</sup> as reported in eq. (5).

$$\text{RCS} = \frac{(K/S)_{\text{sample}}}{(K/S)_{\text{reference}}} \cdot 100 \quad (5)$$

RCS determination is an indirect method to have an idea of the pigment dispersion inside the matrix: the higher RCS values, the better dispersion can be achieved.<sup>21</sup>

### Rheological Characterization

Dynamic rheological measurements were carried out by using a Dynisco Polymer LCR 52M capillary rheometer, at a chamber temperature of 260°C and in a shear rate ( $\dot{\gamma}$ ) interval between 100 and 10,000 s<sup>-1</sup>. Pelletized samples were previously dried in a vacuum oven at 120°C for 24 h, to ensure a moisture content <0.1%.<sup>22</sup> The samples were maintained in the rheometer for two different residence times (3 and 23 minutes), in order to detect if the pigment promotes the thermo-oxidative degradation of the matrix or if it tends to agglomerate at prolonged processing times. These intervals were chosen according to the requirements of the industrial processing of polyamides. In particular, a time of 3 minutes is required to completely melt PA6 in the rheometer oven at 260°C, while an interval of 23 minutes is the typical residence time at elevated temperature for a melt spinning process. Apparent viscosity curves ( $\eta_{\text{app}}$ ) were fitted through the Cross equation<sup>23,24</sup> (eq. (6)), in order to determine the values of the zero-shear rate viscosity ( $\eta_0$ ), and of the  $C$  parameter, that is related to the cohesive energy of the particles under shear stresses<sup>5</sup>:

$$\eta_{\text{app}} = \eta_{\infty} + \frac{\eta_0 - \eta_{\infty}}{1 + (C\dot{\gamma})^m} \quad (6)$$

where  $\eta_{\infty}$  is the viscosity at the second Newtonian plateau at elevated shear rates and  $m$  is a coefficient related to the slope of the pseudo-plastic interval of the rheological curve.

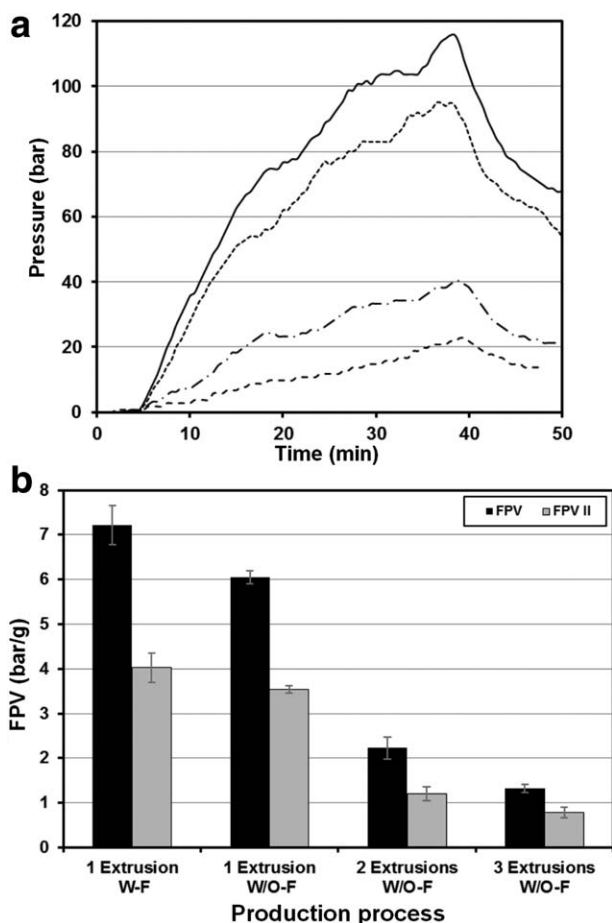
Relative viscosity tests were performed through an Ubbelohde viscometer according to ISO 307 standard on monoconcentrated masterbatches chips. About 0.4 g of samples were previously dried for 30–60 minutes in oven at 90°C and solubilized at 50°C with sulfuric acid (purity 95.7%), at a concentration of 5 and 10 g L<sup>-1</sup>. The solution was then put in a water bath at 25°C for 20 minutes and then tested at the same temperature. In this way, it was possible to extrapolate Intrinsic Viscosity ( $\eta_i$ ) values of the samples.<sup>25</sup>

### Chemical Characterization

End groups analysis on extruded pellets was performed in order to investigate the effect of the different processing conditions on the chemical properties of the monodispersed masterbatches. These tests were carried out by using a Mettler DL50 automatic titrator coupled with an electronic voltmeter. About 0.8 g of samples were solubilized in 20 mL of 2,2,2 trifluoroethanol (TFE) at 55°C. —NH<sub>2</sub> groups titration was performed at 25°C through a HCl 0.02 N solution, while —COOH titration was conducted with a NaOH 0.02 N solution. Considering that the adopted testing methods and the relative parameters have been optimized, and the absolute error associated to each measurement is in the order of 1 mmol<sub>eq</sub> g<sup>-1</sup>.

## RESULTS AND DISCUSSION

Dioxazine violet is the most used violet pigment in the paint and plastic industry, but it is also one of the most problematic products in terms of dispersion in the polymer matrix. In order to reduce its tendency to clog the filtration system during the production and the melt spinning process, it was produced in four different conditions (see Table III). Filter-Test analysis was thus performed in order to evaluate the clogging power of the pigments. In Figure 3(a), the pressure curves of the four monoconcentrated violet masterbatches are reported. Three distinct regions can be detected: (i) a first plateau region in which the pressure remains constant due to the flow of neat (i.e. unfilled) PA6 matrix, (ii) a second zone characterized by an important pressure increase due to the masterbatch flow through the filter, and a third region (iii), characterized by a final pressure drop due to the flowing of neat PA6, with the breakage of less stable agglomerates deposited on the filter surface. In Figure 3(b) the mean values of FPV and FPVII for each processing condition are summarized. The filtration process showed a negative effect in term of clogging power because the monoconcentrated violet masterbatch, produced without filter, is characterized by significantly lower FPV and FPVII values. For this reasons, the industrial filtration should be removed from the industrial layout of these products. An increase of the number of extrusions (i.e. of the specific mechanical energy applied to the system) during the production allows to markedly reduce the clogging power of the masterbatch and thus to decrease the aggregation tendency of the violet pigments. For instance, with a third extrusion it is possible to reduce the FPV of about 82% with respect to the monoconcentrated violet masterbatch produced in the standard way (i.e. one extrusion with filtration). Moreover, a change of the processing conditions reduces the aggregates dimension without altering the clogging physical mechanism. This is demonstrated by the fact that the relative variation

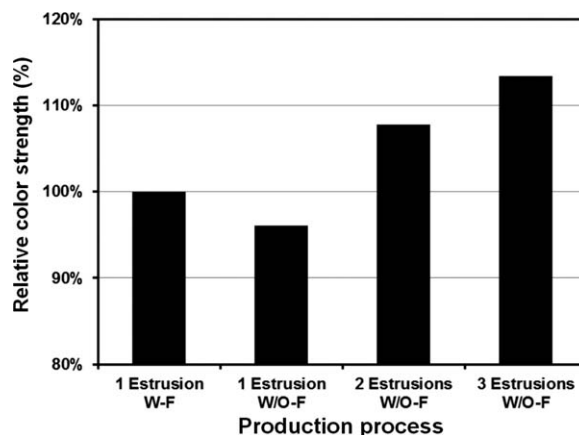


**Figure 3.** (a) Representative Filter Test curves and (b) FPV and FPV II values of monoconcentrated masterbatches with different processing conditions. (—) 1 Extrusion W-F; (----) 1 Extrusion W/O-F; (- - -) 2 Extrusions W/O-F; (- - -) 3 Extrusions W/O-F.

between FPV and FPV II values remains fairly constant for all the tested samples (around 45%).

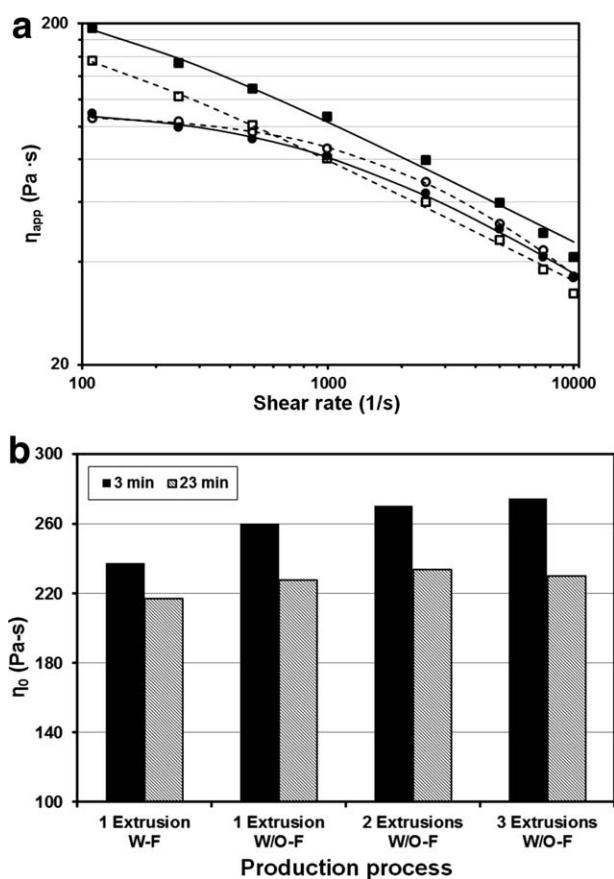
The RCS values of monodispersed violet masterbatches, evaluated taking the 1 E-W-F as a reference, are summarized in Figure 4. It can be noticed that the filtration process slightly reduces the RCS of the masterbatch, but the second and the third extrusions determine an interesting positive effect on the product color strength. For instance, a third extrusion allows to increase the RCS of about 20% with respect to the monoconcentrated violet masterbatch obtained with one extrusion without filtration. This is probably due to the better pigment dispersion within the polymer matrix due to the higher energy involved in the process. These considerations are in accordance with the results obtained through Filter-Test. Economically speaking, an improvement of RCS leads to a reduction of production cost and a higher masterbatch stability.

Figure 5(a) shows the rheological curves of the neat PA6 and of the monoconcentrated violet masterbatch after 3 and 23 minutes of residence time at 260°C in the rheometer. For as concerns neat PA6, its viscosity is slightly increased after 23 minutes of residence time at shear rate higher than 1000 s<sup>-1</sup>, because of the post-condensation reaction that occurs inside the

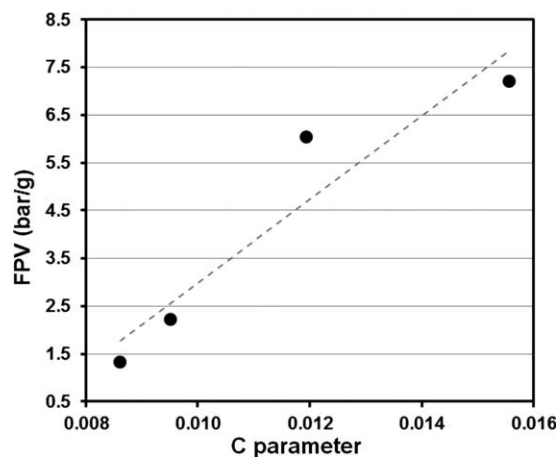


**Figure 4.** Relative Color Strength (RCS) of monoconcentrated violet masterbatches prepared with different processing parameters.

rheometer.<sup>26–28</sup> The presence of dioxazine violet pigment produces an important increase of the apparent viscosity of the PA6 at low shear rate because of the reduction of the polymer chain mobility due to the hindering effect promoted by the



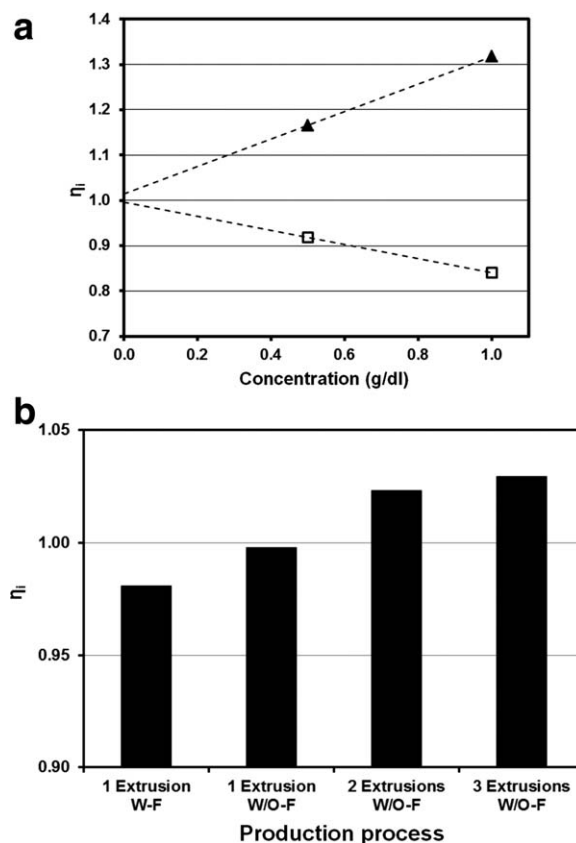
**Figure 5.** (a) Rheological curves of neat PA6 matrix with a residence time of (●) 3 minutes and of (○) 23 minutes, and rheological curves of 1 Extrusion W/O-F monodispersed violet masterbatch with a residence time of (■) 3 minutes and (□) 23 minutes. (b) Zero shear rate ( $\eta_0$ ) values of monoconcentrated masterbatches with different processing conditions, obtained from the fitting of the rheological curves through the Cross model (eq. 6).



**Figure 6.** Correlation between FPV and C parameters of monoconcentrated violet masterbatch.

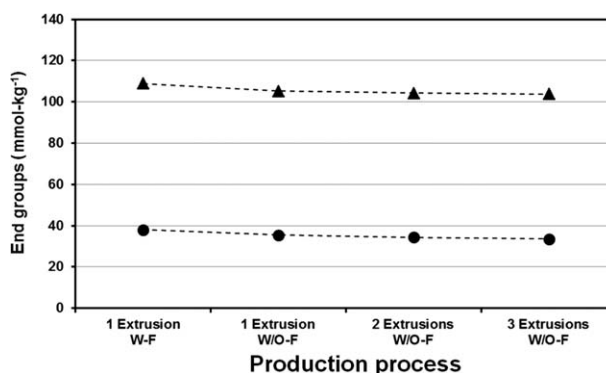
pigment aggregate into the matrix. The rheological curve of the monoconcentrated violet masterbatch after 23 minutes is shifted at lower apparent viscosity values. This is due to the thermo-oxidative degradation of the polymer matrix. The viscosity values at zero shear rate ( $\eta_0$ ), obtained through the interpolation of the rheological curves with the Cross equation, are reported in Figure 5(b). The filtration process seems to lower the system viscosity, in fact the masterbatch produced without filter shows higher viscosity values. This is probably due to the elevated shear stresses developed into the filtration system during the production that promote degradative phenomena in the matrix. An increase of the extrusion number leads to an increase of the zero shear rate viscosity. This is probably due to the important reduction of the pigment aggregate dimension and enhancement of dispersity in the matrix. As explained by Cassagnau,<sup>29</sup> better distributed aggregates are more able to link the macromolecules within the aggregates, increasing the chain blocking effect in the polymer matrix. Once again, an increase of the compounding time lead to a systematic reduction of the zero shears rate viscosity values, because of the thermo-oxidative degradation of the matrix. Figure 6 shows the correlation between FPV values, obtained from Filter-Test, and the C parameter, determined through the fitting of rheological curves with the Cross model (eq. (6)). The C parameter, proportional to the bonding energy between the particles under shear flow, is reduced increasing the number of extrusions (i.e. increasing the specific mechanical energy involved in the production process). This is due to the higher degree of pigment disagglomeration for prolonged extrusions. In fact, also FPV can be reduced for repeated extrusions (see Filter-Test analysis). Therefore, a decrease of the clogging power of the monodispersed violet masterbatch for repeated extrusions leads to a proportional drop both of the C coefficient and of the FPV values.<sup>5</sup>

Figure 7(a) shows reduced and inherent viscosity trends obtained from relative viscosity measurements on the solutions of 1 Extrusion W/O-F sample. At zero concentration they converge into the intrinsic viscosity ( $\eta_i$ ), and in Figure 7(b)  $\eta_i$  values of the four samples produced by using different process condition are summarized. The intrinsic viscosity of the



**Figure 7.** (a) Intrinsic viscosity analysis of 1 Extrusion W/O-F masterbatch. (▲) Reduced viscosity and (□) inherent viscosity. (b) Intrinsic viscosity values of masterbatch chips.

monoconcentrated violet masterbatch increases removing the filtration system (in accordance with the rheological measurements), and it further increases upon a second and a third extrusion. Considering that  $\eta_i$  values mainly depend on the molecular weight distribution within the polyamide matrix, the experienced increase of intrinsic viscosity values for repeated extrusions can be tentatively explained considering the post condensation reaction that occurred in the matrix during the production of the monoconcentrated violet masterbatch. It is also possible that the presence of the filler could promote the kinetics of the post condensation reaction.



**Figure 8.** End groups analysis on violet masterbatches with different process conditions. (●) aminic end groups and (▲) carboxylic end groups.

The number of carboxylic and aminic terminal functionalities of the monoconcentrated violet masterbatches, measured through end groups analysis, are shown in Figure 8. According to the rheological and relative viscosity measurements, the number of both carboxylic and aminic end groups is slightly reduced by removing the filtration system and by increasing the number of extrusions. This means that filtration leads to a thermo-mechanical degradation of the matrix, while repeated extrusions promote post-condensation reactions, increasing thus the mean molecular weight of the matrix. Concluding, re-processing of the monodispersed violet masterbatch allows to improve pigments dispersion and to promote the kinetics of post condensation reaction within the matrix.

## CONCLUSIONS

A monoconcentrated violet masterbatch was produced through an extrusion process by mixing a commercial PA6 with dioxazine color pigments. A detailed investigation on the process parameters was performed in order to find the best conditions to reduce the clogging power and thus to increase the color strength. It was demonstrated how increasing the specific mechanical energy applied to the system for pigments dispersion (i.e. increasing the number of the extrusions) the filler dispersion quality was improved, reducing the FPV and increasing the RCS. Moreover, the filtration stage resulted to be an unuseful processing step for the monodispersed violet masterbatch production. Interestingly, a prolonged thermo-mechanical treatment favored post-condensations reactions, as demonstrated by the results of relative viscosity measurements and end group analysis.

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