STUDY ON VARIOUS DISPERSANTS IN PP MASTERBATCHES AND FIBRES MODIFIED BY PROTECTIVE PHOTOLUMINESCENT PIGMENT

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Abstract: *Polypropylene (PP) doesn't contain functional groups; therefore dyeing in the mass by pigments is used in the dyeing of PP fibres. Dispersants are used to improve dispergation, increasing the homogeneity of the masterbatches. In this work, the influence of three types of dispersants on the processability and processing properties of protective photoluminescent pigment of PP masterbatches as well as the effect of dispersants on the resulting structural and mechanical properties of modified PP fibres were studied. Dispersants D1 and D2 (polyethylene waxes) weren't significantly demonstrated in the preparation of masterbatches, while dispersant D3 (N, N-bis-stearyl ethylenediamine) affected the melt flow index of the resulting masterbatches. The modified PP fibres with the protective photoluminescent pigment were prepared from masterbatches and PP by the discontinuous process of the spinning and drawing associated with the false-twist texturing of the fibres. The influence of dispersants on the resulting properties of the fibres didn't manifest itself significantly.*

Keywords: *modified PP fibres, masterbatches, properties, photoluminescent pigment, dispersants.*

1 INTRODUCTION

The development of special, modified, mono- and multi-functional active fibres and textiles characterized by their high functionality, flexibility, diversity and environmentally acceptable production is still a topical issue [1-3]. One of the ways to achieve sophisticated properties of fibres and consequently also of textiles is the use of photoluminescent pigments. Photoluminescent pigments belong to the materials where the excitation is caused by light and can be: fluorescent - with a short light response or phosphorescent - with a long light response [4-6].

Polypropylene (PP) fibres having a nonpolar paraffinic character are generally undyeable by the classical bath-dyeing method and therefore the substantial part of the PP fibre production is colored with pigments (mass dyed fibres) thereby obtaining a permanent functional modifications of fibres [7, 8]. The incorporation of an additive into the fibre mass is almost always preceded by the preparation of a functional masterbatch containing - carrier, additive (pigment) and an appropriate dispersing system [9, 10]. Dispersing system ensures a higher dispergation of the pigment in the fibre mass. A masterbatch is added to main PP stream in a pre-defined volume during the spinning process. The mixture is then melted, homogenized and spun into the form of modified fibres.

This article provides results of the three types dispersants influence on the preparation and properties of photoluminescent pigment masterbatches as well as their influence on the result properties of modified PP fibres. The modified PP fibres with protective photoluminescent pigment were prepared by the discontinuous process of spinning and drawing associated with the false-twist texturing of the fibres.

2 EXPERIMENTAL AND METHODS

2.1 Materials

Isotactic polypropylene (PP) produced by Slovnaft Company with MFI = 27.6 g/10 min (230°C/2.16kg), protective organic photoluminescent pigment (FP) of Radiant Color Company were used, and three types of dispersants: D1 - is a polyethylene wax having medium molecular weight, D2 - is a non-polar high density polyethylene with low molecular weight and the last D3 - is an amide wax of type N,N-bis-stearyl ethylenediamine, all produced by Clariant Corporation.

2.2 Preparation of PP masterbatches

The preparation of PP masterbatches of photoluminescent pigment was carried out on a Werner-Pfleiderer ZDSK-28 twin-screw extruder with a screw diameter ∅ = 28 mm, with a vacuum zone and accessories for premix preparation process.

The premixes consisted of a PP carrier, photoluminescent pigment (FP) and a dispersants D1, D2 and D3 (Table 1). The ingredients of PP premixes were compounded, melted and the resulting extrudates were cooled in water and pelletized.

Table 1 Composition of PP masterbatches

Sample	Concentration of additives [wt.%]				
	PP	FP	dispersants		
			D1	D2	D3
PP/1%FP	99.0	1.0	-	-	-
PP/1%FP/D1	98.7	1.0	0.3	-	-
PP/1%FP/D2	98.7	1.0	-	0.3	-
PP/1%FP/D3	98.7	1.0	-	-	0.3
PP/3%FP	97.0	3.0	-	-	-
PP/3%FP/D1	96.5	3.0	0.5	-	-
PP/3%FP/D2	96.5	3.0	-	0.5	-
PP/3%FP/D3	96.5	3.0	-	-	0.5

2.3 Fibres preparation

The modified PP fibres were prepared from mechanical blends of PP granulated polymer and PP masterbatches using the discontinued process of spinning and drawing associated with the false-twist texturing of the fibres. The undrawn PP fibres on the laboratory spinning line with an extruder diameter of D = 32.0 mm and with constant processing conditions - the spinning temperature of 220°C, spinneret 2x25 holes with diameter 0.3 mm and final process speed of 1500 $m.min^{-1}$ were prepared. Subsequently, drawing associated with false-twist texturing of fibres was performed on the Barmag AFK-U-HTI line under process conditions - drawing ratio DR = 1.69, texturing temperature of 225°C, mechanical speed of 350 $m.min^{-1}$ and D/Y ratio of 1.77.

2.4 Methods used

<u>MFR of masterbatches</u> was evaluated using a Dynisco Kayness capillary rheo-viscometer according to EN ISO 1133-1 Plastics: Determination of melt flow mass index (MFR) and melt flow volume index (MVR) of thermoplastics. Part 1: Standard method.

<u>Filterability (filter pressure value)</u> was evaluated using a filtration single-screw extruder with a screw diameter of 25 mm and pore density of the filtration sieve of 16000 pores per cm^2. The filterability of the dispersion (*F*) is expressed as ratio of an increment of the pressure (Δp) on the filter to a weight unit of the filtrate (*m*) at the definite filtration conditions.

<u>Fibre´s birefringence:</u> The orientation of the segments of macromolecular chains in fibre expresses the level of anisotropy of oriented polymer system (fibre). The total orientation of prepared modified PP fibres was evaluated using polarization microscope DNP 714BI. The refractive indexes of light in the fibre axis ($n_{//}$) and in the perpendicular direction of fibre ($n_{\perp}$) were determined. From the difference of refractive indexes of light, the fibre birefringence was calculated.

<u>Crystallinity</u> β represents the crystalline portion of fibres. In this work DSC-Q20 apparatus TA Instruments was used. The non-isothermal process of analysis was performed. All samples of PP fibres were heated at temperatures from 60 to 260°C at a rate of 10°C.min^{-1} under a nitrogen flow. From melting endotherm of 1st heating of PP fibres the melting enthalpy (ΔH_m) was determined. This value was used for the calculation of crystallinity in PP fibres using equation 1:

$$\beta = \frac{\Delta H_m}{\Delta H_{m,0}} \cdot 100\% \qquad (1)$$

where $\Delta H_{m,0}$ = 198.11 $kJ.kg^{-1}$ is the melting enthalpy of PP with the 100% crystallinity.

<u>Mechanical properties of fibres</u> were measured in accordance with the EN ISO 2062 and fineness was measured in accordance with the EN ISO 2060. The equipment of Instron 3345 tensile tester for the measurement of mechanical properties (Young´s modulus, tenacity and elongation at the break) was used.

3 RESULTS AND DISCUSSION

3.1 Preparation of masterbatches and determination of their properties

The performed experimental work proved the possibility of preparation of PP masterbatches containing 1 wt.% and 3 wt.% of protective photoluminescent pigment using dispersants D1 - D3. The process of preparing masterbatches (Table 1) was technologically stable without interrupting the strings entering the pelletizer. The uniformity of the granules was satisfactory for all PP masterbatches of the pigment, without undercuts and without an increased proportion of dust particles. It follows that the selected type of polypropylene is a suitable polymeric carrier for the preparation of PP masterbatches. To prevent agglomeration of the pigment particles in the matrix under the preparation of PP masterbatches the dispersants D1 - D3 were used.

In terms of technological stability of the preparation of PP pigment masterbatches, the following twin screw extruder parameters were monitored - melt temperature, screw speed, drive load of the twin screw extruder, output rate and string pelletizing speed (Table 2).

Table 2 Parameters of PP masterbatches preparation

Sample	Melt temperature [°C]	Screw speed [rpm]	Drive load [%]	Output rate [kg/h]	Pelletizing speed [m.min^{-1}]
PP/1%FP	249	270	62	4.2	12
PP/1%FP/D1	249	270	61	4.1	12
PP/1%FP/D2	249	270	63	4.3	12
PP/1%FP/D3	298	270	73	4.3	12
PP/3%FP	274	270	63	4.1	12
PP/3%FP/D1	273	270	58	4.2	12
PP/3%FP/D2	273	270	72	4.4	12
PP/3%FP/D3	268	270	66	4.2	12

It was found that due to the dispersant D3 being at its lower content of 0.3 wt.% in the PP/1%FP/D3 masterbach, the melt temperature and the drive load of extruder increased compared to parameters of remaining masterbatches with a 1% FP content. This is probably due to the formation of agglomerates in the melt. On the other hand, at its higher content of 0.5 wt.% (PP/3%FP/D3 masterbatch) there is a decrease in the melt temperature compared to the melt temperature of remaining 3% FP masterbatches. In this case, the drive load is comparable to other masterbatches. This is partly related to the higher MFR of the masterbatch PP/3%FP/D3 as well as to the lower filter pressure value of mentioned masterbatch (Table 3). The effect of dispersants D1 and D2 did not manifest itself significantly in the preparation of concentrates.

By evaluating the processing properties of PP masterbatches (Table 3), it was found that the addition of dispersant D3 (masterbatches PP/1%FP/D3 and PP/3%FP/D3) causes an increase in melt flow index and a reciprocal decrease in melt viscosity of PP masterbatches compared to masterbatches PP/1%FP and PP/3%FP without dispersant content. If necessary, there is therefore a realistic assumption of the possibility of regulating the melt flow index; resp. melt viscosity of PP concentrates by dispersant type in masterbatch. Dispersants D1 and D2 do not have a significant effect on the processing properties of masterbatches. Low coefficients of variation 1.68%-2.32% demonstrate the high flow uniformity of PP masterbatches of the protective photoluminescent pigment.

For PP masterbatches containing 3 wt.% of photoluminescent pigment, the filter pressure value is significantly lower compared to the FPV of 1% PP masterbatches (Table 3). This is probably due to the higher content of low molecular weight substances (pigment, dispersant) in the polymer matrix of 3% masterbatches, which leads to its dilution, as well as due to the different ratio of photoluminescent pigment (FP): dispersant (D). In the case of 1% masterbatches the FP:D content ratio is 3.3:1.0, while in the case of 3% masterbatches the FP:D ratio is 6.0:1.0, which means that in 1% masterbatches on the same amount of dispersant accounts for a smaller number of pigment particles. This can result in an excess of dispersant, which can lead to agglomeration of the pigment particles in the PP melt and thus to an increase in the filter pressure value of the masterbatches. From the above, it is clear that 3% masterbatches are more suitable for fibre preparation because they have a low filter pressure value, which demonstrates a high degree of pigment dispersion in the PP matrix.

PP masterbatches with 1% content of photoluminescent pigment will be used to prepare fibres containing 0.01 wt.% FP and PP masterbatches with 3% content of FP will be used to prepare fibres containing 0.1 wt.% FP pigment in the PP matrix. The purpose was to minimize the amount of once remelted polymer in the preparation of the fibres.

Table 3 Processing properties: melt flow index (MFR), viscosity (V), filter pressure value (FPV) and associated variation coefficients (CV_X) of prepared PP masterbatches

Sample	MFR[a)] [g/10 min]	CV_{MFR} [%]	Viscosity [Pa.s]	CV_V [%]	FPV [MPa/kg]
PP/1%FP	26.05	1.68	299.5	1.7	< 398
PP/1%FP/D1	27.10	2.31	286.6	2.3	< 401
PP/1%FP/D2	26.88	1.85	288.7	1.8	< 415
PP/1%FP/D3	28.25	2.27	274.7	2.3	< 433
PP/3%FP	27.81	1.91	280.3	1.9	< 128
PP/3%FP/D1	27.60	2.02	281.2	2.0	174
PP/3%FP/D2	26.16	1.81	276.5	1.8	< 140
PP/3%FP/D3	29.79	2.32	255.7	2.3	112

[a)] 230°C/2.16 kg (τ = 19500 Pa)

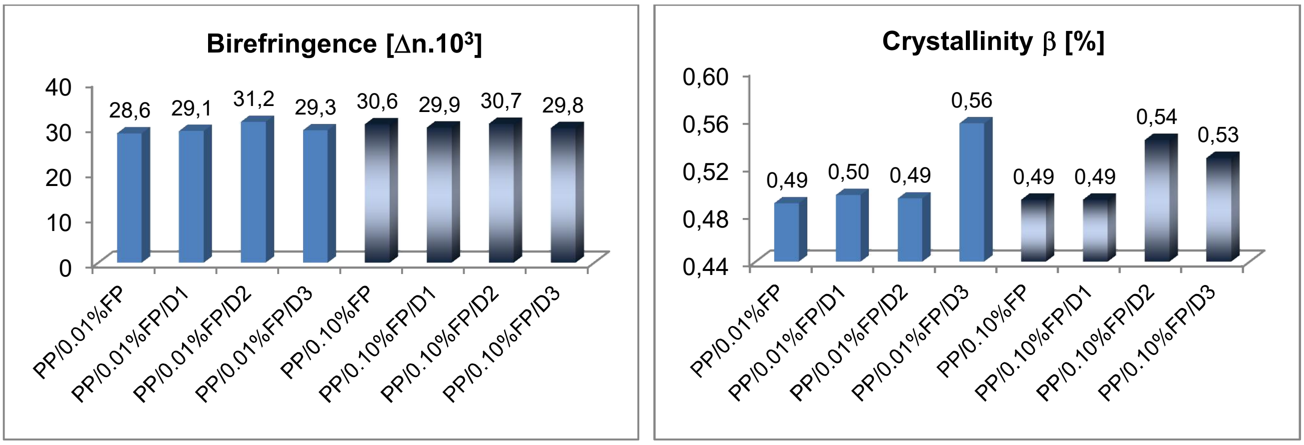
3.2 Preparation of modified PP fibres and determination of their properties

Spinning process of the prepared PP blends was stable in all cases and the prepared fibres corresponded to the quality required for discontinuous shaping and drawing of the fibres. Fibres containing 0.01 wt.% and 0.1 wt.% of the protective photoluminescent pigment were prepared from mechanical blends of 1% and 3% PP masterbatches and polypropylene. The resulting structural parameters and mechanical properties of the false-twist textured PP fibres are shown in Figures 1-3.

The birefringence of the modified PP fibres is in the range of 0.0286 - 0.0312 and remains practically unchanged due to the dispersants (Figure 1a). Crystallinity of the fibre with a dispersant D3 content was increased by 14% compared to the fibre without the dispersant at a photo-luminescent pigment content of 0.01 wt.%, indicating that it could partially act as a nucleating agent. At higher FP contents of 0.10 wt.%, the crystallinity of concentrates containing dispersants D2 and D3 is 10% higher compared to the fibre without dispersant content, which may be partly due to the effect of dispersants and partly to measurement error (Figure 1b).

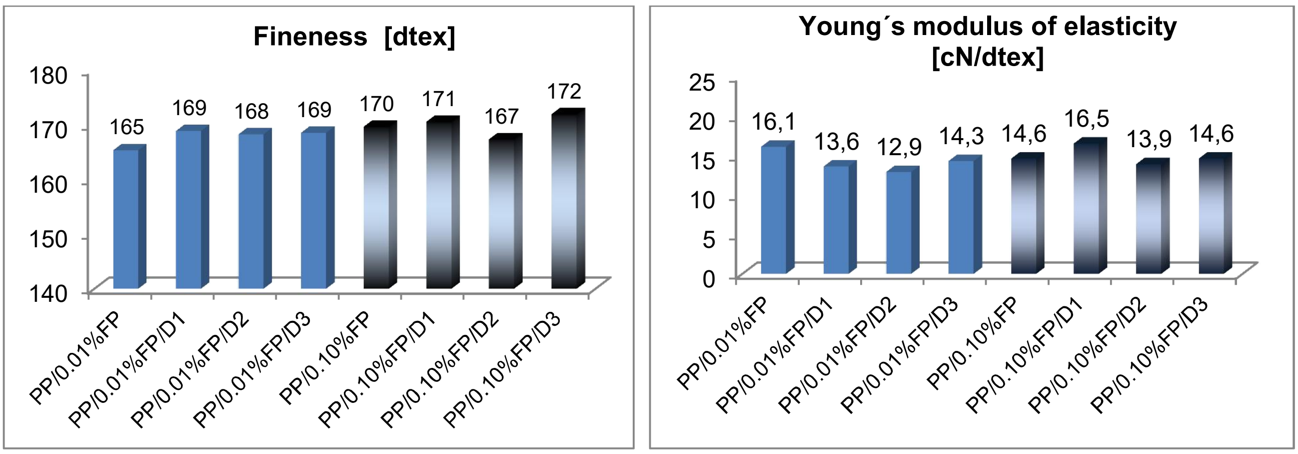
Fineness of the false-twist textured PP fibres with the content of photoluminescent pigment is in the range of 165 - 172 dtex, which means that the dispersants do not affect the fineness and the resulting deviations are caused by a failure of the bursting device (Figure 2a).

Young's modulus of elasticity was decreased by dispersants (max. 20%) in the fibres containing 0.01 wt.% of photoluminescent pigment (Figure 2b). In this case, the diluting effect of the dispersants was manifested too. Fibres with a higher pigment content of 0.10 wt.% did not show this effect; probably all of the dispersant was used to coat the pigment particles.



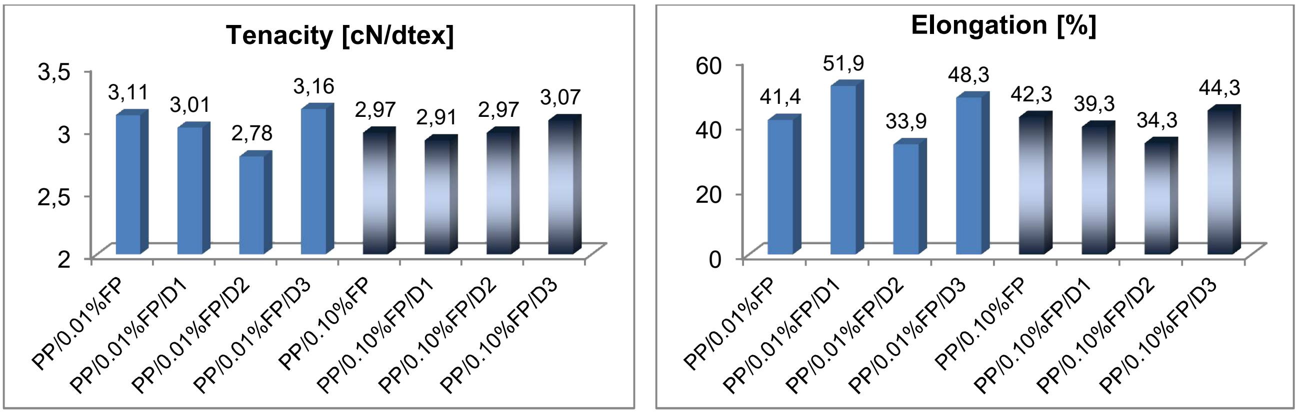
a) b)

Figure 1 Comparison of structure parameters: a) birefringence and b) crystallinity of false-twist textured PP fibres containing photoluminescent pigment (FP) and dispersants D1, D2 and D3 as well as fibres without dispersants



a) b)

Figure 2 Comparison of a) fineness and b) Young's modulus of false-twist textured PP fibres containing photoluminescent pigment (FP) and dispersants D1, D2 and D3 as well as fibres without dispersants



a) b)

Figure 3 Comparison of mechanical properties: a) tenacity and b) elongation of false-twist textured PP fibres containing photoluminescent pigment (FP) and dispersants D1, D2 and D3 as well as fibres without dispersants

Tenacity of the most modified fibres containing dispersants does not change significantly; the difference compared to fibres without dispersants does not exceed 10%. The lowest mechanical properties were measured for the PP/0.01%FP/D2 fibre (Figure 2b and Figure 3). The decrease in mechanical properties of the PP/0.01%FP/D2 fibre is probably related to the low molecular weight character of the dispersant.

Small differences in the structural parameters and mechanical properties of the fibres are related to the low content of masterbatch in the spinning mixture and the associated low content of pigment and dispersants in the fibres.

4 CONCLUSION

In the first part, the influence of dispersants D1, D2 and D3 on the preparation of masterbatches of protective photoluminescent pigment (FP) was studied. Masterbatches with 1.0 wt.% FP and 0.3 wt.% dispersant and 3 wt.% FP and 0.5 wt.% dispersant as well as masterbatches without dispersants with 1.0 wt.% and 3.0 wt.% FP were prepared. Low coefficients of variation 1.68 - 2.32% of melt flow index and viscosity demonstrate high flow uniformity of PP masterbatches. The effect of dispersants D1 and D2 itself did not prove significantly in the preparation of masterbatches, while the dispersant D3 (N, N-bis-stearyl ethylenediamine) influenced the melt temperature during the preparation of the masterbatches as well as the melt flow index of the resulting masterbatches. The filter pressure value is significantly lower for PP masterbatches containing 3 wt.% of photoluminescent pigment, compared to the filterability of 1% PP masterbatches. This is probably due to the higher content of low molecular weight substances (pigment, dispersant) in the polymer matrix as well as due to the different pigment-dispersant ratio.

In the second part, the influence of dispersants on the preparation of false-twist textured fibres as well as their influence on the structural parameters and mechanical properties of the fibres was studied. The spinning process of the prepared PP blends was stable in all cases. Dispersants have been found not to have a significant effect on the structural parameters and mechanical properties of fibres, what it is probably related to the final low content of pigment and dispersants in the resulting fibres.

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