

Anton Marcinčin,
Marcela Hricová,
Jaroslav Lučivjanský*

Slovak University of Technology in Bratislava
Faculty of Chemical and Food Technology
Department of Fibres and Textile Chemistry
Radlinského 9, 812 37 Bratislava, Slovakia
Telephone: +421 2 52968598
E-mail: anton.marcincin@stuba.sk

*Fibrochem-Chemosvit a.s.
Štúrová 101, 059 21 Svit, Slovakia

Influence of the Rheological Properties of Pigment Concentrates on Unevenness of Polypropylene Spun-dyed Fibres

Abstract

In this paper, the influence of selected rheological parameters of polypropylene pigment concentrates on the external and internal unevenness of polypropylene spun-dyed fibres was investigated. For external unevenness of pigmented fibres the coefficient of variation of fibre diameter was used, and for internal unevenness the coefficient of variation of fibre tenacity was used. The dependencies of fibre unevenness on viscosity and other rheological parameters of pigment concentrates were evaluated. The lower difference between concentrate viscosity and viscosity of basic polypropylene is more suitable for the process of mixing polymer components, and for the homogeneity and evenness of polypropylene spun-dyed fibres.

Key words: pigment concentrates, rheological properties, fibre diameter, unevenness, polypropylene fibres, spun-dyed fibres.

by new kind of pigments [4,5]. Extensive work in the area of nanocomposite polymer materials and fibres has been carried out in recent years [6]. It is necessary to realise that the application of solid particles for fibre modification on the production scale is not a simple process, as it depends greatly on processing both the additives (pigments, fillers, dispersants) and their concentrate forms. Compatibiliser dispersants are often needed, particularly for polyolefins, to enhance the degree of the dispersion of solid particles in the polymer before spinning [7].

Some previous papers reveal that the processing of pigment concentrates and the basic properties of spun-dyed fibres are related to the degree of pigment dispersion and distribution in the polymer melt, and to the miscibility of solid particle concentrates with basic polymer. A quantitative evaluation of the degree of pigment dispersion is possible using standard methods, such as microscopic methods. An original method, called 'filterability' for the indirect characterisation of particle size in concentrates, was also developed. As the same experimental works have shown, this method is

also very sensitive regarding the mutual (surface) interactions of the solid particles and other components in the dispersion [8]. Furthermore, the rheological properties of pigment concentrates have been studied; familiar equations such as Ostwald & de Waele's, Mooney's, Casson's, Cross's and others, as well as the parameters of these equations for characterising the behaviour of pigment dispersion in oligomers and polymer, have been used [9].

Evaluating the technological miscibility of pigment concentrate with polymer directly in technological conditions is very difficult and leads to questionable results. Heterogeneity of the blend on several levels can be obtained in the blending process, and the mutual interactions of components leads to pseudobalance in the structure and morphology of spun-dyed fibres. The mutual miscibility of the polymer carrier and the basic polymer is expected as a rule, but the strong attractive interaction of pigment particles in concentrate will prevent their perfect distribution in the polymer-concentrate blend. Non-uniformity in the particle (concentrate) distribution can be expected

Introduction

The modification of chemical fibres by solid particles in mass and the processing of polymers in fibre production are still commonly used at the present time because of the development of many new special fibres based on composite polymers containing solid additives on the micro- and nano-scale, such as antibacterial fibres [1], electrically conductive fibres [2] and fibres with magnetic fillers [3], as well as fibres pigmented in mass

Table 1. List of concentrates and fibres used.

No	Concentrates		No	Fineness of multifilaments, dtex	Fineness of monofilaments, dtex
	Pigment	c, %			
1CO	C.I.P. White 7	20	1a	84/25 × 2	1.68
			1b	167/32 × 2	2.61
2CO	C.I.P. Yellow 180	25	2	110/33 × 2	1.67
3CO	C.I.P.: White 7, Black 7, Blue 15:3	15	3	56/33	1.69
4CO	C.I.P.: White 7, Black 7, Blue 15:3	15	4	72/25 × 2	1.44
5CO	C.I.P. Black 7	20	5	110/33 × 2	1.67
6CO	C.I.P. Black 7	20	6	72/25 × 2	1.44
7CO	C.I.P. Blue 15:3	20	7	110/33 × 2	1.67

ted in spun-dyed fibres. Two kinds of fibre parameters which can be related to this non-uniformity in morphology are external and internal unevenness. Both kinds can be exposed using suitable methods, for example, by statistical variance in fibre diameter (external) and by variance in mechanical properties (internal).

While investigating the polyethylene terephthalate black pigment concentrates and spun-dyed fibres, the relations between filterability and rheological parameters, which were obtained for pigment dispersion in oligomeric polyolefins were verified. The very important proportionality between the filterability and viscosity of the concentrates was confirmed. Furthermore, the previous assumption that the miscibility of concentrates and polymers plays an important role in pigment distribution in the fibres at an optimum degree of pigment dispersion in concentrates was confirmed. In addition, the dependence between the rheological parameters and the external unevenness (diameter) of PET spun-dyed fibres was established [10].

In this paper, the processing of the polypropylene pigment concentrates expressed by their rheological properties and by both the external and internal unevenness of PP spun-dyed fibres was investigated. Commercial inorganic and organic pigments were used in our experimental work. The processing of pigments was evaluated by using the rheological measurements. The miscibility of PP concentrates with PP was estimated by an indirect method of both the internal and external unevenness of spun-dyed fibres. Pigment concentrates in PP carriers and PP spun-dyed fibres were prepared and selected using common industrial production.

Experimental

Material used

Polypropylene PP TI 924, MFI=30 g/10 min, Slovnaft a.s., SK. Polypropylene concentrates and spun-dyed fibres represent the commercial product of Fibrochem-Chemosvit a.s., SK. The basic characteristics of the pigment concentrates and PP spun-dyed fibres are listed in Table 1. The concentrates used in this work were selected with regard to their different behaviour in spun-dyed fibre production of fibres with different linear densities. From this point of view, some

of them were used for the preparation of fibres with different linear density.

Methods used

Rheological properties

A Göttfert capillary rheoviscosimeter with extruder $\phi=20$ cm was used for measuring the rheological properties of PP and PP pigment concentrates. Viscosity within the shear stress of $(10-100)\times 10^3$ Pa and shear rate to 3.5×10^3 s⁻¹ at 260°C was measured. We used the Newton equation

$$\tau = \eta \cdot \dot{\gamma}$$

and the Ostwald-de Waele power law

$$\tau = K \cdot \dot{\gamma}^n$$

where:

τ - shear stress,

$\dot{\gamma}$ - shear rate,

η - dynamic viscosity,

K - coefficient,

n - deviation from the Newtonian flow power-law index,

for evaluating the basic rheological characteristics of PP and concentrates.

The agglomeration coefficient λ was calculated from the straight-line dependence

$$\log \eta = \log \eta_\infty + \lambda \cdot \tau^{-1}$$

where η_∞ is the viscosity of dispersion at $\tau \rightarrow \infty$ [9].

Unevenness of spun-dyed fibres

External unevenness: The coefficient of fibre diameter variation was used to express the fibres' external unevenness. The diameter of individual fibres was measured within the length of 350 cm at 10 randomly selected cross-sections for 10 individual fibres. The CV_D (coefficient of variation) was evaluated from 100 measurements, using standard equations.

Internal unevenness: The structure unevenness of the PP fibres was indirectly evaluated using measurements of the mechanical properties of fibres, tenacity and elongation. The Instron type 1112 was used for measuring the fibres' mechanical-physical properties. The distance between the clamps were as follows: 10 cm, speed of clamp at measurement: 50 cm min⁻¹. The coefficient of fibre tenacity variation CV_T was evaluated from 100 measurements, and the standard equation for calculating CV_T was used.

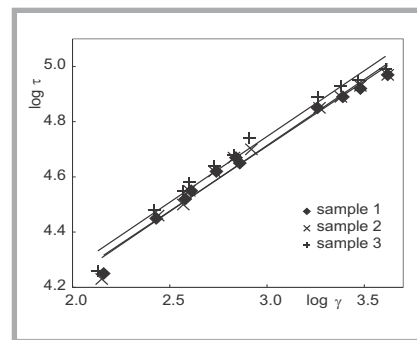


Figure 1. Dependence of the $\log \tau$ on $\log \gamma$ for PP TI 924 at 260°C.

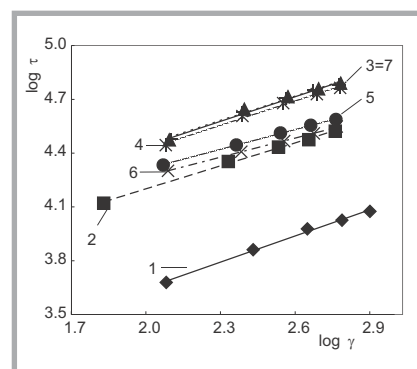


Figure 2. Dependence of the $\log \tau$ on $\log \gamma$ for pigment concentrates in polypropylene at 260°C: 1 - C.I.P. White 7; 2 - C.I.P. Yellow 180; 3 - C.I.P.: White 7, Black 7, Blue 15:3; 4 - White 7, Black 7, Blue 15:3; 5 - C.I.P. Black 7, 6 - C.I.P. Black 7, 7 - C.I.P. Blue 15:3.

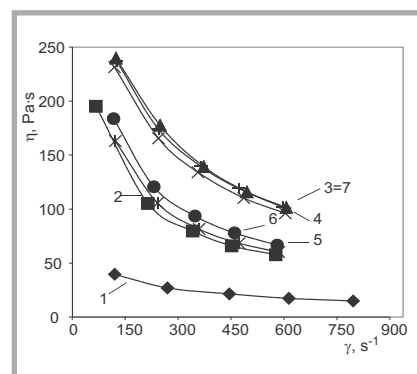


Figure 3. Dependence of viscosity η on share rate γ for pigment concentrates in polypropylene at 260°C: 1 - C.I.P. White 7; 2 - C.I.P. Yellow 180; 3 - C.I.P.: White 7, Black 7, Blue 15:3; 4 - White 7, Black 7, Blue 15:3; 5 - C.I.P. Black 7, 6 - C.I.P. Black 7, 7 - C.I.P. Blue 15:3.

However, unevenness of dyeing is important for the application of fibres and textile products and, like other parameters and properties of fibres (such as elongation at break), it can be used to estimate the fibres' internal unevenness. In our work, only the CV of tenacity and of the fibre diameter were selected for estimating the unevenness of the fibres.

Results and Discussion

The straight-line dependence

$$\log \tau = f(\log \dot{\gamma})$$

for PP TI 924 demonstrates the reliable measurement of the rheological properties of polymer melt by the Göttfert extrusionmeter, as well as the validity of the Ostwald-de Waele equation on the wide scale of the shear rate (Figure 1).

Figures 2, 3 and Table 2 indicate the great differences in the rheological properties of PP pigment concentrates. The highest viscosity of C.I. Pigment Blue concentrate corresponds with the high 'coefficient of agglomeration λ ' at a relatively lower deviation from Newtonian flow, in comparison with other types of concentrates ($n=0.46$) (Figure 4, Table 2). The same concentration of C.I. Pigment Black 7 in the PP carrier provides a lower viscosity value and the highest deviation from Newtonian flow ($n=0.36-0.37$). The lowest viscosity was measured for the concentrate of inorganic pigment (C.I. Pigment White 7) and azopigment C.I. Pigment Yellow 180 despite having the highest concentration (25%). Relatively high viscosity was discovered in concentrates based on pigment mixture (white, black and blue), in spite of the fact that these concentrates have the lowest concentration of pigment (15%). In any case, the rheological properties of concentrates are strongly

influenced by the type of pigments and the composition of the pigment mixture. It can be assumed that the difference in the viscosity of the PP concentrates can significantly influence their technological miscibility with basic PP polymer. In our previous work, this assumption was confirmed for PET black concentrates and PET pigmented fibres [10].

The size of micro-volumes with higher and lower concentration of pigments in the PP+pigment concentrate blend influences the unevenness and distribution of the components in coloured PP during the spinning process, and leads to external and internal unevenness of the pigmented fibres. The results in Table 3 indicate both a difference in fibre diameter unevenness expressed by the coefficient of variation CV_D (external unevenness) and a difference in structure unevenness, expressed by the coefficient of variation of the fibres' tenacity CV_T (internal unevenness).

Mixing the pigment concentrates with basic polymer in melt and laminar flow conditions using one screw extruder is the most frequently used method for pigmenting the polymer melt before spinning on an industrial scale. In spite of these unfavourable conditions, a high degree of pigment dispersion and its distribution in polymer melt are expected.

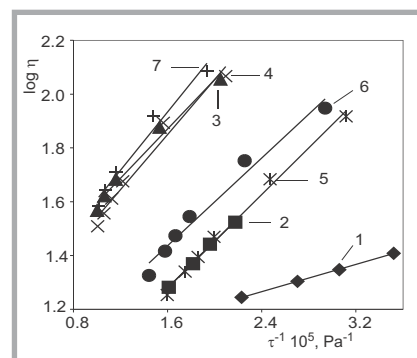


Figure 4. Dependence of $\log \eta$ on τ^{-1} for pigment concentrates in polypropylene at 260°C: 1 - C.I.P. White 7; 2 - C.I.P. Yellow 180; 3 - C.I.P.: White 7, Black 7, Blue 15:3; 4 - White 7, Black 7, Blue 15:3; 5 - C.I.P. Black 7; 6 - C.I.P. Black 7; 7 - C.I.P. Blue 15:3.

ted. With regard to the low mixing and homogenisation efficiency of the simple one-screw extruder, the rheological properties of pigment concentrates related to the rheological properties of basic polymer are very important for the high degree of pigment dispersion in the fibres. In general, mixing the concentrate and polymer can be accepted as the mixing of two partially miscible liquids with high viscosity. The disintegration of concentrate chips is supported by the diffusion of polymer chains through an 'interphase' polymer-concentrate, and the diffusive decrease in pigment concentration is created at the interphase point. It can be assumed that the final mixture is represented by micro-volumes with higher and lower concentrations of pigments in coloured polymer. The low mixing efficiency or unsuitable rheological properties of concentrates led to the creation of insufficiently-dispersed "flocules", which represent the deformed micro-volumes mentioned above with a diameter size of several micrometers.

Comparing the CV_T and CV_D in Table 3 shows the independence of these quantities. CV_D depends mainly on the rheological unevenness of micro-volumes due to the difference in the concentration of components. Additionally, CV_T depends strongly on the supermolecular structure of the fibres, which is also influenced by the pigments' nucleating effect [11,12].

The characteristic dependencies of the external and internal unevenness of PP spun-dyed fibres on viscosity and on the coefficient λ of pigment concentrates confirmed our assumption concerning the dependence between the rheological behaviour of concentrates and the une-

Table 2. Basic rheological characteristics of PP and PP pigment concentrates at 260°C.

No.	Composition	Viscosity, Pa·s			n	λ
		$\dot{\gamma} = 150 \text{ s}^{-1}$	$\dot{\gamma} = 300 \text{ s}^{-1}$	$\dot{\gamma} = 500 \text{ s}^{-1}$		
PO	PP TI 924	138	105	86	0.61	0.74
1CO	C.I.P. White 7	36	25	19	0.49	0.13
2CO	C.I.P. Yellow 180	126	85	63	0.43	0.43
3CO	C.I.P.: White 7, Black 7, Blue 15:3	223	153	116	0.46	0.72
4CO	C.I.P.: White 7, Black 7, Blue 15:3	210	144	109	0.46	0.78
5CO	C.I.P. Black 7	143	92	66	0.36	0.54
6CO	C.I.P. Black 7	158	102	74	0.37	0.64
7CO	C.I.P. Blue 15:3	221	152	115	0.46	0.85

Table 3. Tenacity T and diameter D of PP spun-dyed fibres, and coefficients of variation of these values.

No.	Undrawn		Drawn		Annealed		Undrawn		Drawn	
	T, cN/dtex	CV_T , %	T, cN/dtex	CV_T , %	T, cN/dtex	CV_T , %	D, μm	CV_D , %	D, μm	CV_D , %
1a	1.56	3.05	4.67	1.80	4.89	1.49	-	-	21.5	4.74
1b	1.39	3.12	3.95	1.24	4.07	1.19	39.6	6.82	26.4	4.05
2	1.66	2.74	4.25	1.72	4.41	0.90	30.5	4.65	20.8	4.25
3	1.94	3.21	3.54	3.05	3.52	2.92	17.4	7.24	15.3	4.54
4	1.73	1.57	3.99	2.27	4.05	2.15	27.2	3.81	19.2	6.57
5	1.75	3.41	3.76	1.36	3.97	1.45	28.6	4.74	20.6	3.36
6	1.50	3.20	3.90	2.00	4.05	1.12	29.4	5.42	18.9	3.63
7	1.68	2.83	3.42	1.82	3.51	1.58	28.1	6.13	20.9	9.71

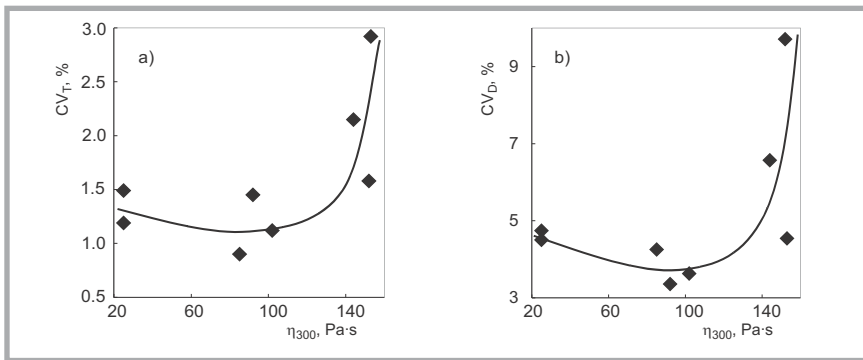


Figure 5. Dependence of variation coefficient of: a) tenacity CV_T (%); b) diameter CV_D (%); of spun dyed annealed PP fibres on η ($\dot{\gamma} = 300 \text{ s}^{-1}$) of pigment concentrates in polypropylene at 260°C .

venness of the pigmented fibres (Figures 5 and 6). The geometrical and structural unevenness of fibres exhibit dependence on both the viscosity η and the coefficient of the agglomeration λ of concentrates. The greater difference between the concentrate and the PP viscosity leads to lower mixing efficiency. This means that both higher and lower concentrate viscosity, compared to the viscosity of non-coloured PP, lead to a lower technological miscibility of concentrate

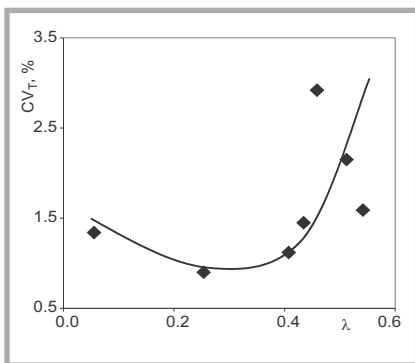


Figure 6. Dependence of variation coefficient of the tenacity of spun dyed annealed PP fibres on agglomeration coefficient λ for pigment concentrates in polypropylene at 20°C .

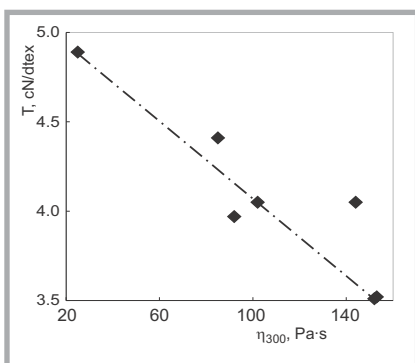


Figure 7. Dependence of tenacity T (cN/dtex) of spun dyed annealed PP fibres on η ($\dot{\gamma} = 300 \text{ s}^{-1}$) of pigment concentrates in polypropylene at 20°C .

and polymer. The term ‘technological miscibility’ expresses the degree of distribution of micro-volumes of dispersed phase and matrix in the fibres at defined blending conditions. The shape of the dependencies in Figures 5 and 6 is characterised by a slight minimum of CV_D (CV_T). These minima of unevenness of spun-dyed fibres appear at a concentrate viscosity approximately equal to that of the basic PP polymer. It means that the best conditions for mixing polymer and concentrates resulting from the minimum of external and internal unevenness of pigmented fibres were found for the similar viscosity of both polymer and concentrates. It can be assumed that the ‘interface interaction’ polymer – (where the concentrates are similar to polymer+polymer or concentrate+concentrate) positively influences the mixing process.

The unevenness of pigmented PP fibres influences not only the variance in the mechanical-physical properties of spundyed fibres but also their absolute values. Figure 7 reveals that there is indirect proportionality between the tenacity of spundyed fibres and the viscosity of pigment concentrates. The dependence is in harmony with the perception of the mixing mechanism of concentrate with polymer, and with the assumed morphology and unevenness of the pigmented fibres. The higher is the technological miscibility of concentrates with polymer, the higher is the tenacity of fibres, and the lower the internal and external unevenness of the pigmented fibres.

Conclusion

- The rheological properties of pigment concentrates significantly depend on not only the pigment concentration

but also on the kind and structure of the pigments.

- The viscosity of pigment dispersion in PP is a suitable parameter for characterising concentrates from the point of view of miscibility with a non-pigmented polymer.
- The dependencies of external (CV_D of fibre diameter) and internal (CV_T of fibre tenacity) unevenness of pigmented PP fibres on concentrate viscosity with a minimum of these parameters were established. The minimum corresponds with the most convenient conditions for the technological miscibility of PP and PP concentrates.
- Drawn and annealed pigmented PP fibres are more convenient for evaluating general unevenness in comparison with undrawn fibres.



Acknowledgement

The support of the Slovak grant agencies APVT (grant 20-010102) and VEGA (grant 1/9147/02) is appreciated.

References

1. Jeong S. H.: PA6/Ag antibacterial nanocomposite fibres, In *Proceedings: Polymer Fibres 2002, UMIST, Manchester, UK, 2002*.
2. Gubin S. P.: *Colloid and Surfaces A - Phys. Chem. Eng. Aspects* 202, 2002, p. 153.
3. Caramaro L.: New functional yarns obtained by additives and modification of polymers during extrusion spinning, In *Proceedings: 41 International Man-Made Fibres Congress, Österreichisches Chemiefaser Institut, Dornbirn 2002, Austria*.
4. Erk P.: From crystal to colloids, designing new pigmentary organic colorants, in *8th Int. Conf. on Dyes and Pigments, Colorchem 2000, VUOS Pardubice, CZ, 2000*.
5. Iqbal A. et al.: Latent pigments - a new concept in pigment technology, in *7th Int. Conf. on Dyes and Pigments, Colorchem 1998, VUOS Pardubice, CZ, 1998*.
6. Alexandre M., Dubois P.: *Material Sci. and Eng.* 28, 2000, p. 1.
7. Pavlíková S. et al.: *J. Appl. Polym. Sci.* 89, 2003, p. 604.
8. Marcinčin A., Krištofič M.: *Fibres and Textiles in EE* 2 (3), 1994, p. 38.
9. Marcinčin A.: *Progress in Polym. Sci.* 27, 2002, p. 853.
10. Marcinčin A., Ujhelyiová A., Brejka O.: *Vlákna a Textil (Fibres and Textiles)* 10 (3), 2003, p. 109.
11. Broda J., Wlochowicz A.: *European Polymer Journal* 36, 2000, p. 1283.
12. Broda J.: *Polymer* 44, 2003, p. 1619.

Received 01.03.2004 Reviewed 14.07.2004