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Dyeing Kinetics and Colouristic Properties of Blend PP/PES Fibres

Abstract
The aim of this work was the study of the dyeability of blended polypropylene/polyester (PP/PES) fibres. Blended PP/PES fibres contain various polyesters - polyethylene terephthalate (PET), polybuthylene terephthalate (PBT), polytrimethylene terephthalate (PTT) and a blend of these polyesters. The fibres were dyed with C.I. Disperse Blue 79 and C.I. Disperse Violet 95 at 98°C. The dyeing kinetics and colouristic properties of these fibres were investigated. In addition, the influence of different contents of individual PES was also studied.

Key words: *blend PP/PES fibres, disperse dye, dyeing kinetics.*

Introduction

Polypropylene (PP) is a very important polymer for the production of synthetic fibres due to its good physical and chemical properties as well as relatively low price. Recently, a lot of research has dealt with the modification of PP for engineering applications and improvement of some properties. The improvement of the dyeability of PP fibres bath-dyed belongs among these properties.

One of these modifications, which improves some properties and dyeability of PP, is the preparation of fibre-forming polymer blends [1 - 7]. A polymer blend, which can increase the affinity of PP to disperse dyes, is blending PP with different polyesters (PES) [8, 9]. Apart from an improvement in dyeabilty, the blend of these polymers attains higher sorption properties and higher elasticity [2]. Polypropylene and polyester are thermodynamically immiscible, and therefore blending two or more polymers usually results in a multiphase blend, instead of homogenous materials. The formation of fibrillar phase morphology is affected by the compatibility of the polymer blendand technological process of preparation, i.e. blending history, blend ratio, viscosity of individual polymer compound and share rate. Hence, many researchers have focused on the control of morphology and interfaces of immiscible polymer blends in order to improve their compatibility. Bataile et al. [10] reported that PP/PET blends without compatibilisers exhibit weak interactions between the two phases and the mechanical properties showed lower values than individual PP and PET. The option of mixing and spinning conditions as well as the addition of suitable compatibilizers can increase uniformity in blend phase morphology and evenness of fibre properties at a lower viscosity of the PET dispersed in the PP matrix [11, 12]

The morphology of the blended PP/PES fibres influences the dyeability of these fibres. Whereupon for the dyeing process of these fibres it is important to provide a uniform distribution of the PES particles in the PP matrix because the molecules of the disperse dye penetrate through the full cross section of blended PP/PES fibres, but the molecules of the dye are mainly localised in the PES particles. The uniform size and distribution of the PES particles in the PP matrix form a higher specific surface for the adsorption of disperse dyes from dyebath into fibres [9].

The transport of disperse dyes in PP/PES fibres from a bath can be described in four stages as follows:
a) dissolution of the dye molecules from a dispersed state into a monomolecular dissolved state;
b) transport through a bulk solution to near the surface;
c) diffusional transport through any boundary layer surrounding the fibres and partition to the immediate surface of the fibre;
d) diffusion within the fibre.

In a well-optimised dyebath, the last step is rate-determinion . Most dye diffusion studies so far have usually determined the overall rate of dyeing. In these studies the diffusion coefficient is determined from the time-dependant dye-uptake [13 - 15].

The study of the dyeability of blended PP/PES fibres is the main aim of this paper. We prepared blend fibres containing different types of PES compounds (PET, PBT and PTT) and blends of PES compounds (PET/PBT, PET/PTT, PBT/PTT and PET/PBT/PTT). For the dyeing of blended PP/PES fibres, Disperse Blue 79 and Disperse Violet 95 were used. The composition of dyebath was used as for PET fibres. We focused on the influence of the individual type of PES and its ability to increase the affinity of blended PP/PES fibres to disperse dyes. The influence of PES additives dispersed into a PP matrix on the dyeability and diffusion of disperse dyes are presented.

Experimental

Synthetic fibres

The following polymers were used for the preparation of the blended PP/PES fibres:
- Polypropylene Tatren TG 920 (PP), Slovnaft, a.s., Bratislava, MFI = 10.5 g/10 min ;

Table 1. Composition of the blend PP/PES fibres.

Types of fibres		Contents of individual compound in the blended PP/PES fibres, %				
		PP TG 920	PET	PBT	PTT	Licowax E
PET	A	-	100	-	-	0.12
PP/PET	B	94.34	5.54			0.12
PP/PBT	C	94.34		5.54		0.12
PP/PTT	D	94.34			5.54	0.12
PP/PET/PBT	E	94.36	1.64	3.88		0.12
PP/PET/PTT	F	94.36	1.64		3.88	0.12
PP/PBT/PTT	G	94.36		3.88	1.64	0.12
PP/PET/PBT/PTT	H	94.40	1.88	1.8	1.8	0.12

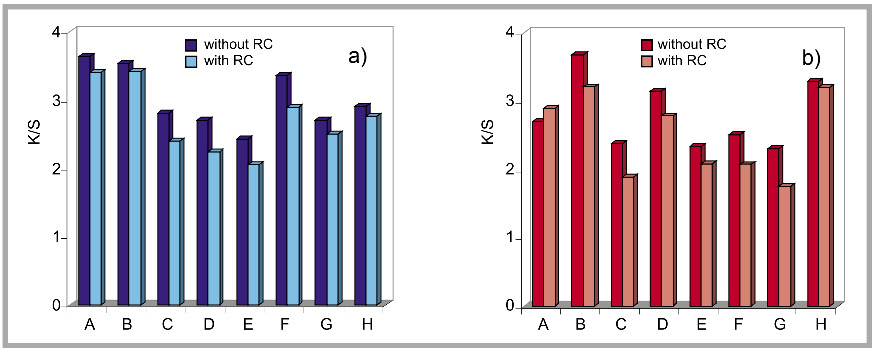

***Figure 1.** The dependencies of K/S on the type of blended PP/PES fibres dyed with Disperse Blue 79 (a) and Disperse Violet 95 (b) at 98 °C. **Remark:** A, ... H as in Table 1.*

- Polyethylene terephthalate PET (PET), Slovenský Hodváb, a. s., Senica, IV = 0.5 l.g^{-1} ;
- Polybuthylene Terephthalate Celanex N 2000 (PBT), Ticona Engineering Polymer, MFI =19.8 g/10 min;
- Poly(trimethylene terephthalate) (PTT) - Du Pont Co - $\eta(\gamma = 100\ s^{-1})$ = 260 Pa.s;
- Licowax E (LiE) – polyester (montane) wax, Ciba Specialty Ltd.

The blended PP/PES fibres was prepared in two steps - preparation of the PES concentrates and preparation of the blended PP/PES fibres. The composition of blended PP/PES fibres is in Table 1.

Disperse dyes

- C.I. Disperse Blue 79
- C.I. Disperse Violet 95

Dyeing

Dyeing conditions

In order to remove the lubricants, the fibres were washed in a bath of 1.5 g.l^{-1} Slovapon and 1 g.l^{-1} Na_3PO_4 at 75°C for 20 min.

The fibres were dyed using a laboratory dyeing machine - Ahiba ↑↓ AG CH 4127 Birsfelden (Switzerland). The following bath composition was used: dispersant 1 g.l^{-1} Kortamol NNO, 2 g.l^{-1} $(NH_4)_2SO_4$, 0.17 g.l^{-1} Texavin and disperse dye 1% o.w.f. The fibres were dyed at 98°C.

Reduction clearing

The dyed fibres were washed in a solution consisting 3 ml.l^{-1} NaOH 38°Be, 1.5 g.l^{-1} Slovapon and 2 g.l^{-1} $Na_2S_2O_4$, at 75°C for 20 minutes.

Methods of analysis

The kinetics of the disperse dyes exhaustion from bath into the PET and PP/PES fibres was evaluated upon an increase (decrease) of dye concentration in the fibres (in bath) during the dyeing process. The dyeing process of the? blended PP/PES fibres was finished at time intervals 3, 5, 10, 15, 20, 25, 30, 50, 70 and 90 min. The quantity of exhausted dye on the fibre was estimated from the absorption of dye solution measured at its λ_{max} and from the calibration curve. The dependence of the exhaustion of dye on time was used for the calculation of the dyeing rate constant (K) and diffusion coefficient (D). The dyeing rate was determined from Vickerstaff's hyperbolic equation [16, 17] (1):

$$c_t = K \cdot t \cdot c_\infty^2 / (K \cdot t \cdot c_\infty + 1) \qquad (1)$$

Diffusion coefficients D were obtained from Hill's empirical equation [13, 18, 19]. The principle of calculation for the apparent diffusion coefficient from Hill's equation is the assumption of the identity of the half-dyeing time $t_{1/2}$ ($t_{1/2}$ is the time required for a fibre absorbing half the quantity of dye absorbed in a state of equilibrium) and half-time diffusion. The diffusion coefficient was calculated from the equation (2):

$$D_{Hill} = 6.324 \times 10^{-2} \cdot K \cdot c_\infty \cdot r^2 \qquad (2)$$

where:
r - radius of fibre, m
D - diffusion coefficient, $m^2 \cdot s^{-1}$
K - dyeing rate constant from Vickerstaff's equation, s^{-1}
c_t - concentration of dye in fibre in the time t, $mg \cdot g^{-1}$
c_∞ - concentration of dye at the moment of state of equilibrium ($mg \cdot g^{-1}$).

Results and discussion

Dyeability of blended PP/PES fibres

The blended PP/PES fibres, which contained 5.54 wt. % of PET, PBT, PTT and blends of these polyesters, were dyed from bath at a temperature of 98 °C with C.I. Disperse Blue 79 and C.I. Disperse Violet 95. The dyeability of the blended PP/PES fibres was evaluated on the basis of colour strength (K/S). The dependences of K/S on the composition of the blended PP/PES fibres are shown in the Figure 1 a-b. The results show that the affinity of disperse dyes to the blended PP/PES fibres is affected by the content and type of PES additive dispersed in the PP matrix.

The highest value of K/S was reached in the blended PP/PES fibres, which contained 5.54 wt.% of PET and was dyed with C.I. Disperse Blue 79. The K/S of the blended PP/PBT/LiE and PP/PTT/LiE fibres reached about 23 - 25% lower values of K/S than PET fibres. PET and PTT dispersed in the PP matrix appeared to be an optimal blend of polyesters (Figure 1.a, blended PP/PET/PTT/LiE fibre). The value of K/S for this fibre reached similar K/S to that of the PET and PP/PET/LiE fibres and the K/S was about 20% higher than the K/S of blended PP/PTT/LiE fibre. The positive influence of PTT on the dyeability of blended PP/PET/PTT fibre can be caused by the suppression of crystallinity and an increase in their deformation ability in comparison with PET and PBT. It can improve the sorption of dye into blended PP/PES fibres. The K/S of the blended PP/PBT/PTT and PP/PET/PBT/PTT fibres were comparable with the K/S of the blended fibres which contained 5.34 wt% of PBT or PTT.

When dyeing with C.I. Disperse Violet 95, the highest K/S was also measured for the blended PP/PET/LiE fibre. Actually, the K/S of these blended PP/PES fibres had a higher value than the K/S of PET fibre. Blended PP/PES (PP/PTT/LiE and PP/PET/PTT/LiE) fibres, which contain PTT compound have higher affinity to C.I. Disperse Violet 95 than blended PP/PBT/LiE and PP/PET/PBT/LiE fibres. On the other hand, a blend using all of PESs (PET, PBT and PTT) creates a suitable homogeneous phase, which is dispersed in the PP matrix as PES particles, for the fixation of Disperse Violet 95. There were reduction cleaning (RC) decreases of K/S in all investigated blend PP/PES fibres. The lower loss of dye after reduction cleaning was reached using C.I. Disperse Blue 79 for all the blended PP/PES fibres than using C.I Disperse Violet 95. The blended PP/PES fibres, which contained PET and a blend of PET/PBT/PTT, provide better fixation of disperse dye than other blended PP/PES fibres. The mutual effects of the PET/PBT/PTT blend was observed on the dyeability of these fibres.

Kinetics of dyeing process of blended PP/PES fibres

The dependencies of dye uptake (in mg·g-1) on the dyeing time for C.I. Disperse Blue 79 and C.I. Disperse Violet 95 are shown at the Figures 2 and 3. The amount of exhausted dye for both dyes is increased with dyeing time. The dependencies of dye uptake confirm previous results. The amounts of exhausted dye in blended PP/PES fibres depend on the composition of these fibres.

Results obtained from dyeing PET and blended PP/PES fibres with C.I. Disperse Blue 79 show that the temperature of 98 °C is not satisfactory for the ideal colouring of PET fibre (Figure 2.a). All the blended fibres attained a higher dye uptake than PET fibre (Figure 2). It means that this dyeing temperature is not sufficient for the achievement of an equilibrium state in the dyeing of PET fibres. The influence of the individual type of polyester on the dyeability of blended fibres is shown in Figure 2. The highest amount of the exhausted dye from bath was reached in the fibres which contained 5.54 wt. % of PET and blend of PET/PTT (1.64/3.88) and the lowest in the blended PP/PBT fibre. The amount of the exhausted dye on the fibres is about 3 mg·g-1. The dyeability of blended PP/PES fibres containing two types of polyesters (PET/PBT

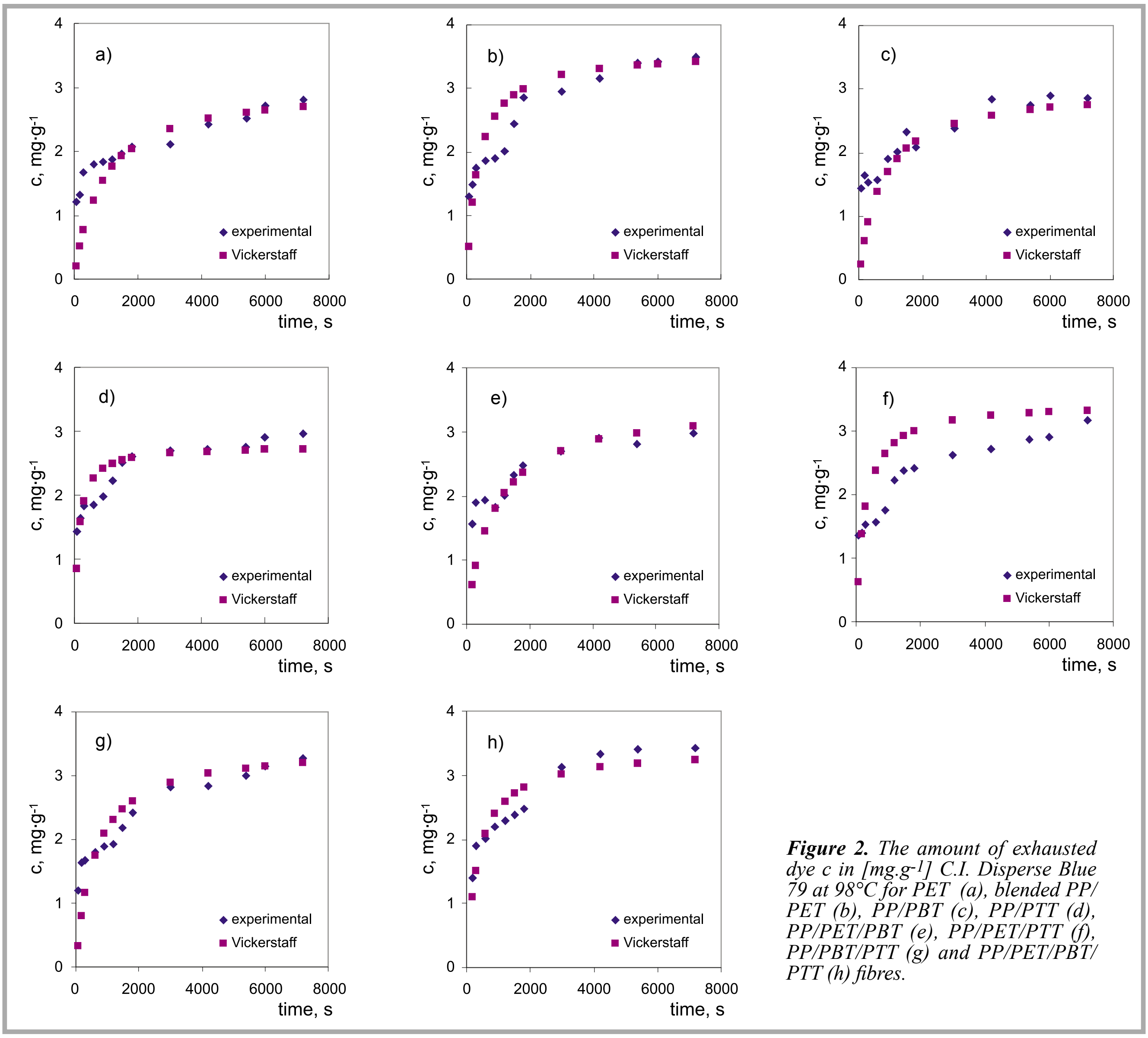

Figure 2. The amount of exhausted dye c in [mg.g-1] C.I. Disperse Blue 79 at 98°C for PET (a), blended PP/PET (b), PP/PBT (c), PP/PTT (d), PP/PET/PBT (e), PP/PET/PTT (f), PP/PBT/PTT (g) and PP/PET/PBT/PTT (h) fibres.

or PET/PTT) is affected by the dominant PES component.

Using the dye C. I. Disperse Violet 95, the amount of exhausted dye for blended PP/PES is within the range up to 2 mg·g^{-1} (Figure 3). The Blended PP/PET and PP/PTT fibres attained the highest dye uptake of all the fibres. Lower dye uptake of C.I. Disperse Violet 95, in comparison with C.I. Disperse Blue 79, can be evoked by a different molecular structure of dye as well as size of the particles.

The dyeing process of blended PP/PES fibres using both disperse dyes can be described by the following steps - disperse dye is absorbed from bath on the surface of blended PP/PES fibres, then the dye penetrates from the surface into the blended fibres, where the disperse dye is mainly absorbed by dispersed PES particles and interphase of PP and PES. For the description of the dyeing process of blended PP/PES fibres from bath, the Viskerstaff's and Hill′s models were used. Calculated and experimental results are in the Figures 2 and 3 and in Table 2 (see page 140). From the dependencies (Figures 2 and 3) it is possible to observe, that both models (Vickerstaff and Hill) are suitable for evaluation of the kinetic process. In both circumstances calculated curves partially copy experimental points. These models were used for the evaluation of rate constant (*K*) and diffusion coefficient (*D*) for PET and PP/PES fibres coloured at 98 °C. The highest value of diffusion coefficient was reached for the blended PP/PTT/LiE and PP/PET/PTT/LiE fibres dyed with C.I. Disperse Blue 79 and for the blended PP/PBT/LiE and PP/PET/PBT/LiE fibres dyed with C.I. Disperse Violet 95. This is caused by the polymer chain of PTT and PBT because these chains are more flexible than that of PET. The diffusion of dye molecules into the dispersed particles of PTT or PBT in the PP matrix of blended fibres could be faster than into PET particles but fixation of disperse dyes is better in blended PP/PES fibres which a contain PET compound (Figure 1).

The dyeing rate constants and diffusion coefficients define the rate of process dyeing but they do not characterise the quality exhaustion of dye on fibres and ability of individual fibres to dye. The exhaustion of dye's very good ability as well as its fixation on the textile fibre or fabric depends on: affinity of dyes to fibres, concentration of dyes in bath, temperature and time of dyeing and textile auxiliaries. The results obtained confirm

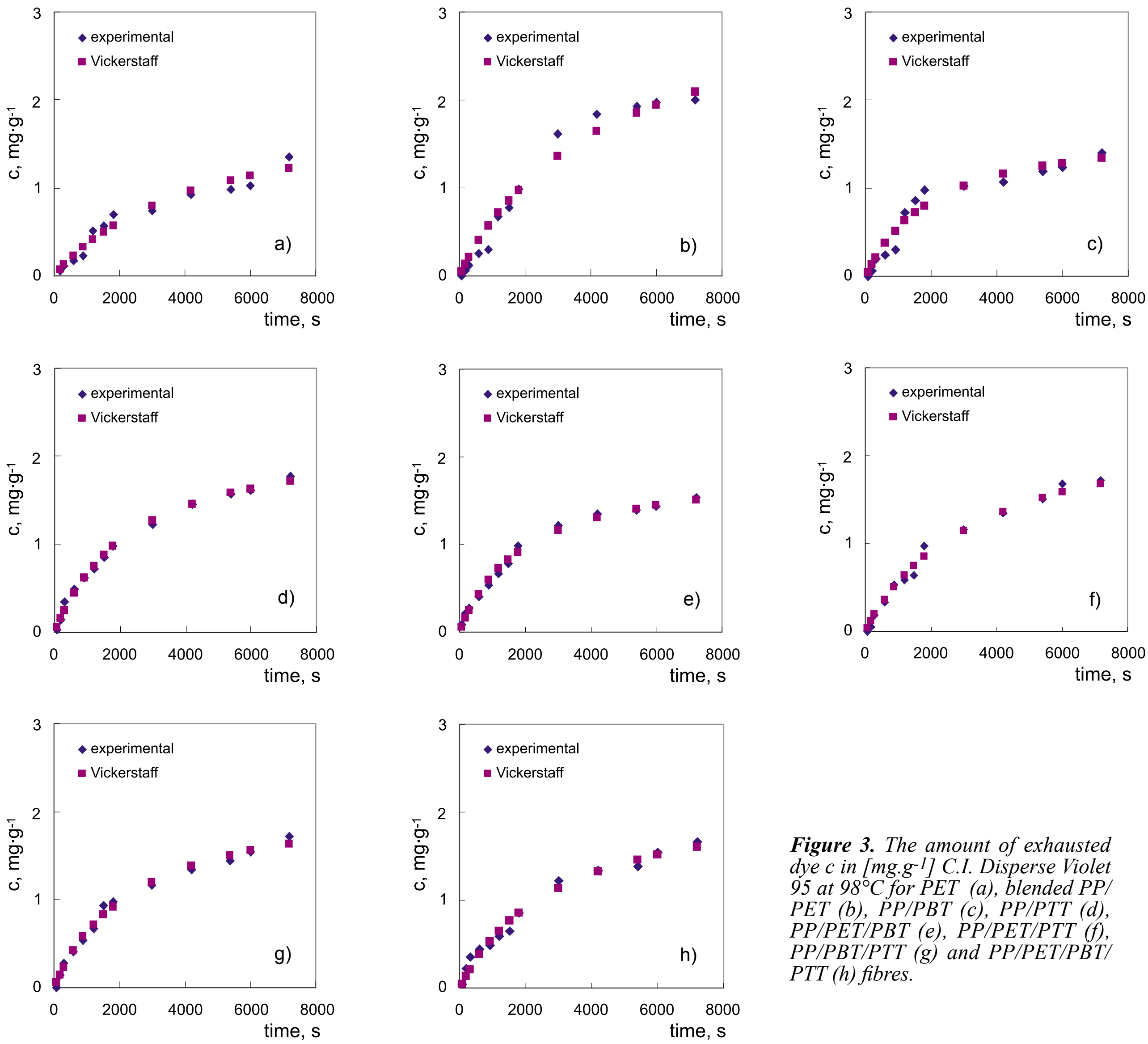

***Figure 3.** The amount of exhausted dye c in [mg.g^{-1}] C.I. Disperse Violet 95 at 98°C for PET (a), blended PP/PET (b), PP/PBT (c), PP/PTT (d), PP/PET/PBT (e), PP/PET/PTT (f), PP/PBT/PTT (g) and PP/PET/PBT/PTT (h) fibres.*

Table 2. Diffusion coefficients (D) and dyeing rate constants (K) of blended PP/PES fibres dyed with C.I. Disperse Blue 79 and C.I. Disperse Violet 95.

Blended PP/PES fibres	C.I Disperse Blue 79		C.I Disperse Violet 95	
	$D_{Hill}·10^{14}$, $m^2·s^{-1}$	$KV·10^4$, s^{-1}	$D_{Hill}·10^{14}$, $m^2·s^{-1}$	$KV·10^4$, s^{-1}
PET A	4.93	3.8	1.06	1.1
PP/PET/Li 94.34/5.34/0.12	16.1	7.8	1.29	0.7
PP/PBT/Li 94.34/5.34/0.12	7.06	4.7	2.30	2.7
PP/PTT/Li 94.34/5.34/0.12	39.2	26.6	2.18	1.8
PP/PET/PBT/Li 94.36/1.64/3.88/0.12	5.84	3.5	2.36	2.5
PP/PET/PTT/Li 94.36/1.64/3.88/0.12	22.2	10.6	1.71	1.1
PP/PBT/PTT/Li 94.36/3.88/1.64/0.12	8.44	4.9	2.00	1.8
PP/PET/PBT/PTT/Li 94.36/1.88/1.8/1.8/0.12	13.0	7.7	1.66	1.5

that PP/PES fibres are sufficiently dyeable from bath by the classical method of using disperse dyes, but it is necessary to optimalise the dyeing condition of certain types of blended PP/PES fibres.

Conclusions

On the basis of the results obtained, the following conclusions can be made:

- the dyeability of all the blended fibres was excellent without streakiness;
- the dyeability of blended PP/PES fibres is influenced by the type of PESs in blend fibres;
- the highest K/S of dyed fibres was reached for the blended PP/PES fibre which contained 5.34 wt. % of PET dyed with both disperse dyes;
- the dyeing kinetics of blend PP/PES fibres dyed with disperse dyes is possible, as described by the Viskerstaff's and Hill's model;
- the highest value of diffusion coefficient was reached for the blended PP/PTT/LiE and PP/PET/PTT/LiE fibres dyed with C.I. Disperse Blue 79 and for the blended PP/PBT/LiE and PP/PET/PBT/LiE fibres dyed with C.I. Disperse Violet 95.

Acknowledgments

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References

1. Afshari M., et al.; Polymer, Vol. 43 (2002) pp. 1331-1341.
2. Marcincin A.; Progress in Polymer Science, Vol. 27(2002) pp. 853-913.
3. Son W., T., et al.; Fibres and Polymers, Vol. 4(2003) pp. 20-26.
4. Marcincin A., Koštialová A., Krištofič M.; Vlákna a textil, Vol. 4(1998) pp. 210-212.
5. Ujhelyiová A., et al.; Vlákna a textil, Vol. 4(1996) pp. 134-140.
6. Sun Y.-J., et al.; Polymer, Vol. 37(1996) pp. 4119-4127.
7. Körmendyová E., et al.; Fibres and Textile in Eastern Europe, Vol. 13(2005) No. 1(49), pp. 20-23.
8. Ujhelyiova A., et al.; Dyes and Pigments, Vol. 72(2007) pp. 212-216.
9. Bolhová E., et al.; Dye Diffusion into Blend Polypropylene/Polyester Fibres evaluated by Confocal Laser Scanning Microscopy, In 6th International Conference - TEXSCI 2007. Liberec, Czech Republic: Technical University of Liberec.
10. P. Bataille S.B., H. P. Schreiber H. P.; Polymer Engineering & Science, Vol. 27(1987) pp. 622-626.
11. Marcinčin A., et al.; Vlákna a textil, Vol. 1(2003) pp. 3-8.
12. Marcincin A., Fibres and textile, Vol. 8(2001) pp. 126-134.
13. McGregor R.; Diffusion and Sorption in Fibers and Films. Academic Press ed. Vol. 1, 1974, London and New York.
14. Etters J.N.; Textile Research Journal, Vol. 64(1994) pp. 406 - 413.
15. Etters J.N.; Kinetics of dye sorption: Effect of Dyebath flow on dyeing uniformity. American Dyestuff Reporter, 1995, January. 3: pp. 38-42.
16. Wang P. Y., Ma J. F.; Dyes and Pigments, Vol. 37(1998) pp. 121-127.
17. Cegarra J., Puente P.; Textile Research Journal, Vol. 37(1967) pp. 343-350.
18. Peters R., H.; The Physical Chemistry of Dyeing. Textile Chemistry. Vol. III. 1975, Amsterdam: Elsievier Scientific Publishing Company.
19. Crank J., Park G. S.; Diffusion in polymers. 1968, Londyn and New Yourk: Academic Press.

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