Available online at www.sciencedirect.com
SCIENCE DIRECT
Dyes and Pigments 72 (2007) 212–216
DYES and PIGMENTS
www.elsevier.com/locate/dyepig

Kinetics of dyeing process of blend polypropylene/polyester fibres with disperse dye

Anna Ujhelyiova*, Eva Bolhova, Janka Oravkinova, Radovan Tiňo, Anton Marcinčin

Slovak University of Technology, Faculty of Chemical and Food Technology, Radlinskeho 9, 812 37 Bratislava, Slovak Republic

Received 28 January 2005; received in revised form 8 February 2005; accepted 19 August 2005
Available online 11 November 2005

Abstract

The dyeing of unmodified polypropylene (PP) fibres by the exhaustion method is characterized by a low affinity of dyes to the PP and by the low colourist parameters (a low colour fastness, a low washing and dry-cleaning fastness) in the dyed fibres. The preparation of polypropylene/polyester (PP/PES) blend of fibres is interesting from the point of dyeability in these fibres from dyebath. Polyester's additive in PP matrix is able to fix disperse dyes and increase the uptake of the dye from a bath. This paper presents the influence of two polyesters (polyethylene terephthalate – PET and polybutylene terephthalate – PBT) in the kinetics of dyeing of PP/PES blend fibres with disperse dye C.I. Disperse Blue 56. The dye uptake, dyeing rate constants, diffusion coefficients and activation energy of PP/PES blend fibres were defined.

Keywords: Blend PP/PES fibres; Disperse dye; Dyeing kinetics

1. Introduction

Dyeing of polypropylene (PP) fibres by the classical method (in a dyebath) gives a very low yield of dyes and low washability. In general, PP fibres are undyeable (from an aqueous dyebath) because of its non-polar, aliphatic structure as well as high crystallinity and high stereo-regularity, which limit the accessibility of dye molecules. It is caused by factors such as:

- insufficient chemical affinity between the fibres and dyes, due to the absence of ionic or polar groups in the polymer chain, so that the retention of dye molecules is only due to the presence of weak Van der Waals' forces,
- the poor accessibility of dyes on the fibres, due to the high degree of crystallinity of PP.

The improvement of dyeability in PP fibres can be reached by chemical and physical modifications of PP [1–4,10,12,16]. The new way for the preparation of PP fibres represents its modification by low molecular weight compounds and nanoparticles [3], polymeric additives (copolymers) with suitable groups fixing certain dyes [4–7], dendrimers and hyperbranched polymers [8,9]. The incorporation of hyperbranched polymer into polypropylene prior to fibre spinning markedly enhanced the dyeability of PP by disperse dyes [5]. In addition, a modification by polymers and polymer mixtures (bicomponent PP/PES and PP/PA fibres) [1,2,10,16] is also largely used for this purpose.

Modification of polypropylene with polyesters for the preparation of a blend PP/PES fibres with majority of PP component is interesting from the point of its changing properties. PES in the blend PP/PES fibres provides an improvement in dyeability by classical exhaust dyeing process, elasticity and sorption properties [1–3]. The created morphology and interface between polymer components in the blend, which can be considered as the third phase, play a predominant role in the improvement of dyeability of the blend PP/PES fibres [4–6].

The current theoretical knowledge about diffusion of dyestuff from a solution into a fibre as well as an effected

* Corresponding author. Tel./fax: +421 2 529 685 98.
E-mail address: anna.ujhelyiova@stuba.sk (A. Ujhelyiova).

0143-7208/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2005.08.026

superstructure of a fibre in its dyeability makes it possible to observe that disperse dyes diffuse primarily into the amorphous regions of blend PP/PES fibres and mainly into the interface. Then PES, which is dispersed in a PP matrix, makes it possible for the creation of a less ordered superstructure of blend PP/PES fibres as well as the creation of the interface being "the third phase" of polymeric system and thereby increasing the dyeability of blend PP/PES fibres. This corresponds with a decrease in total crystallinity of blend PP/PES fibres by the influence of PES in comparison with total crystallinity of original PP and PES components [7,8].

The dyeing process of fibres and/or textiles divides into four consistent processes – diffusion of dye in the solution, adsorption at the fibre surface, diffusion into the fibre and fixation of the dye to the fibre. The diffusion of dye into fibre depends on pH, temperature and uses auxiliary agents as well. In a series of processes joined by successive reactions, the slowest is the one, which determines the rate of the whole process and is, consequently, the one which sets the order of the reaction [9].

Most theoretical equations describing the overall rate of dyeing has been derived by assuming that this is determined by the dye diffusion rate within a fibre [18–23]. Diffusion of dyes into polyester fibres can occur under both infinite and finite dyebath conditions during the dyeing process. In the case of an infinite dyebath, the dye concentration in the bath does not change during the sorption process. In the case of a finite dyebath, the dye concentration at the fibre surface continuously decreases during the sorption process until equilibrium is achieved between the dye concentration in polyester fibres and in the bath [23]. The diffusion rate of dye molecules into polyester fibres from a well-stirred solution is expressed by Wilson's equation for a finite dyebath and by Hill's equation for an infinite dyebath.

The dyeing kinetics of polyester fibres by disperse dyes have been studied by several authors [19–23]. Various mathematical models were used (Vickerstaff [17,21], Patterson and Sheldon [17], Crank [20] diffusion equation, Fick [19] diffusion equation, Hill [21] equation) for the description of the time-dependent dye uptake of PP/PES blend fibres of the dyeing exhaustion process.

This paper presents the influence of two polyesters in dyeing kinetics of PP/PES blend fibres by disperse dye C.I. Disperse Blue 56 (Terasil Blue 3RL).

2. Experimental

2.1. Materials

2.1.1. Synthetic fibres

The following polymers were used for preparation of the blend PP/PES fibres:

- polypropylene tatren TG 920 (PP), Slovnaft, a.s., Bratislava, melt flow index MFI = 11 g/10 min;
- polyethylene terephthalate (PET), Slovenský Hodváb, a.s., Senica, IV = 0.5 l g^{-1};
- polybutylene terephthalate (PBT) Celanex 2000, Ticona Engineering Polymer;
- poly(trimethylene)terephthalate (PTT) with an intrinsic viscosity of IV = 9 l g^{-1} (measured in a 50/50 mixture of methylene chloride and trifluoroacetic acid at 30 °C);
- compatibilizers – oligomeric polyester (OLPET); ethylenedistearamide (EDSA).

Blend PP/PES fibres (PP fibres modified by PET and PBT) were analysed and used for exhaust dyeing (Table 1). The amount of PES dispersed phase in the blend PP/PES fibres was 8 wt.%. The blend PP/PES fibres were prepared in two steps – preparation of PP/PES concentrates and preparation of PP/PES blend fibres. The composition of the used blend fibres is shown in Table 1.

2.1.2. Disperse dyes

- C.I. Disperse Blue 56 (Terasil Blue 3RL).

2.2. Dyeing

From the fibres a lubricant was removed in the bath (1.5 g/l Slovapon A and 1 g/l Na_3PO_4) at 75 °C during 20 min. The fibres were dyed in laboratory equipment AHIBA at temperatures 82, 90 and 100 °C. The dyeing bath contained: 1 g/l Kortamol NNO – dispersant, 2 g/l $(NH_4)_2SO_4$, 3 g/l Na_2SO_4, formic acid pH = 5, disperse dye 1% and dyeing procedure for PET fibres was used.

2.2.1. Dyeing kinetics and the determination in the dye exhaustion

The evaluation of the kinetics in exhaustion process of blend PP/PES fibres is based on an increase (decrease) concentration of dye in a fibre (in a bath) in its dependence from time is significant. The process of dyeing was finished at certain time interval (3, 5, 10, 15, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110 and 130 min). After removal of the fibre from the dyebath, a dyebath was filled up by ethanol into 25 ml. The quantity of exhausted dye in a fibre was estimated indirectly from absorption of the dye solution measured at its λ_{max} in the equipment – SPEKOL and from a calibration curve. The dependence of dye exhaustion on time was used for calculating the dyeing rate constant (K) and diffusion coefficient (D). The dyeing kinetics of polyester with disperse dyes have been studied by several authors – Fick [19], Vickerstaff [17,21], Patterson [17], Crank [20] and Hill [21].

Table 1
Characteristics of the used blend PP/PES fibres

Sample	Composition of fibres		
	PP TG 920 (wt.%)	PES (8 wt.%)	Compatibilizer (1.5 wt.%)
1	90.5	PET	OLPET
2	90.5	PET	EDSA
3	90.5	PBT	EDSA

EDSA – ethylenedistearamide, OLPET – oligomeric polyester.

The rate of dyeing was determined from hyperbolic Vickerstaff's equation:

$$c_t = \frac{Ktc_\infty^2}{Ktc_\infty + 1} \quad (1)$$

The diffusion coefficients D were obtained from Hill's empirical equation. The principle of calculations for apparent diffusion coefficient from Hill's equation is an assumption of identity of half-time in dyeing $t_{1/2}$ ($t_{1/2}$ is the time required for a fibre to absorb half the quantity of dye absorbed in the state of equilibrium) and half-time diffusion. The diffusion coefficient has been calculated by the Eq. (2):

$$D_{\text{Hill}} = 6324 \times 10^{-2} K_{\text{VR}} c_\infty r^2 \quad (2)$$

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

In common with most processes, a rise in temperature increases the rate at which the dye is absorbed. The effects of temperature changes are normally expressed in terms of the activation energy of the process [19]. For this purpose, the changes in diffusion coefficient are described by equation:

$$D = D_0 \exp - \left(\frac{\Delta E}{RT}\right) \quad (3)$$

where ΔE is the activation energy, D is diffusion coefficient at a temperature T, D_0 is a constant independent of temperature,

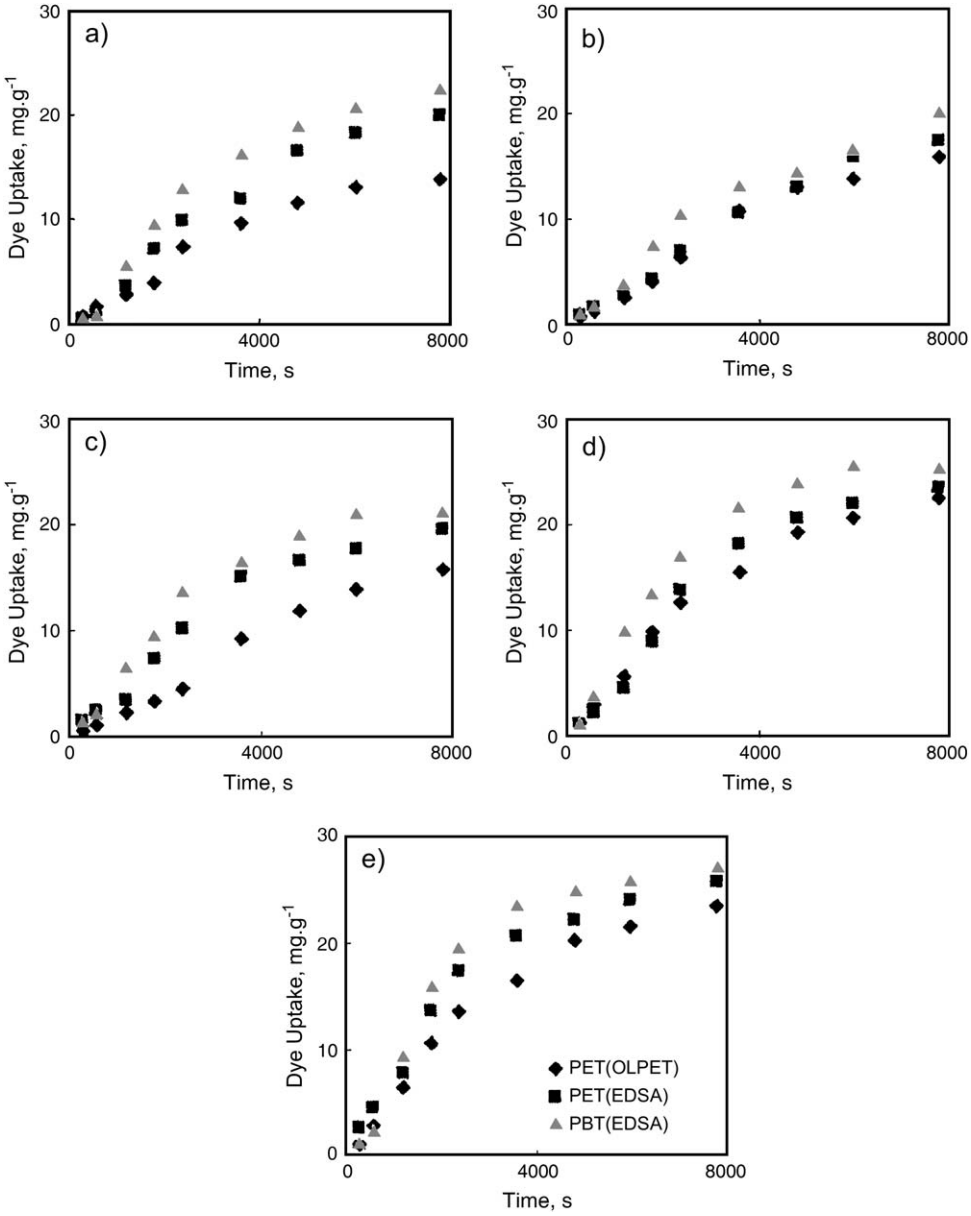

Fig. 1. Dye uptake of C.I. Disperse Blue 56 (Terasil Blue 3RL) at 82 (a), 86 (b), 90 (c), 94 (d) and 100 °C (e) by blend PP/PES fibres.

R is gas constant, T is absolute temperature. ΔE is found from the slope of the graph of ln (D) versus $1/T$. The activation energy is a reflection of the way in which the diffusion coefficient changes with temperature.

3. Results and discussion

The blend PP/PES fibres modified by PET and PBT with compatibilizers EDSA and OLPET were dyed by an exhaust process from the bath by dispersed dye C.I. Disperse Blue 56. The dyeability of these fibres was evaluated as a dependence of the composition of fibres and the dyeing kinetics of the blend PP/PES fibres were investigated as dependence of time (0–90 min) and temperature (82, 86, 90, 94 and 100 °C). The dependence of dye exhaustion on time was used for calculation of dyeing rate constant K, diffusion coefficient D and activation energy E.

The amount of exhausted dyestuff (in mg g^{-1}) C.I. Disperse Blue 56 by blend PP/PES fibres increases with higher time and temperature of dyeing (Fig. 1). Dyestuff is first absorbed on the surface of PP/PES fibres when the state of equilibrium is attained (between absorption and diffusion of dyestuff) as well as when the dyestuff penetrates into fibre pores. The amount of dyestuff exhausted by blend PP/PES fibre and the rate of dye absorption depend on the affinity of dye to the fibre as well as on their chemical structure, on the existence of a sufficient number of active area, amorphous area (macromorphology of fibre), which makes it possible in the dye fixation. The amount of active area increases with an increase in temperature as well as the thermal movement of molecular chains of the various polyesters (PET and PBT) changes with an increase in temperature. This knowledge supports the dyeing of blend PP/PES fibres, where the amount of dyestuff exhausted by blend PP/PES fibres increases with the increase in dyeing temperature (82, 86, 90, 94 and 100 °C). With all temperatures the blend PP/PES fibre modified by PBT (EDSA) has the highest dyeability (Fig. 1a–e). The highest dyeability of PP/PBT blend fibres can be induced by more flexible molecular chains of PBT. It is known that under the same temperature, the thermal movement of molecular chains depends on the hardness and stiffness of the polymer substrate, which is determined by its chemical compositions [24]. The molecular chains of PBT are more flexible than that of PET, then the diffusion of dye molecules into PP/PES blend fibres modified by PBT could be faster than into PP/PES blend fibres modified by PET. The amount of dyestuff exhausted by the PP/PES blend fibres modified by PBT is higher than the amount of dyestuff exhausted by the PP/PES blend fibres modified by PET.

The dyeing rate constant (K) and diffusion coefficient (D) calculated by using the hyperbolic Vickerstaff's and Hill's equations of blend PP/PES fibres dyed by disperse dyes confirm the previous results. The dyeing rate constant (K) and diffusion coefficient (D) increase with increasing dye temperature (Table 2). These results represent that the mobility of polymer chains of the blend PP/PES fibres is greatly increased with increasing temperature. The blend PP/PBT fibre has the highest diffusion coefficient at every temperature in comparison with PP/PET fibres.

Table 2
Diffusion coefficients (D) and dyeing rate constants (K) of blend PP/PES fibres dyed by disperse dye C.I. Disperse Blue 56

Samples	Temperatures of dyeing (°C)	Vickerstaff's model		E (kJ mol^{-1})
		$K \times 10^8$ (s^{-1})	$D \times 10^{15}$ ($m^2\ s^{-1}$)	
PP/PET LFK (OLPET)	82	3.24	0.82	51.9
	86	3.59	1.03	
	90	3.63	1.04	
	94	3.60	1.44	
	100	4.65	1.95	
PP/PET LFK (EDSA)	82	1.66	0.76	94.65
	86	2.30	0.97	
	90	3.27	1.49	
	94	3.27	1.79	
	100	6.02	3.64	
PP/PBT (EDSA)	82	4.15	1.96	51.8
	86	4.94	2.02	
	90	5.53	2.49	
	94	6.99	3.72	
	100	7.15	4.10	

EDSA – ethylenedistearamide, OLPET – oligomeric polyester.

Activation energy describes the dependence of the diffusion on the dyeing temperature and also represents the energy barrier that a dye molecule should overcome to diffuse into the polymer molecules [25]. When the values of the ln (D) were plotted against $1/T$, straight lines were obtained (Fig. 2), whose slopes gave the values of E/R, from which the activation energy in the dyeing of blend PP/PES fibres by disperse dye C.I. Disperse Blue 56 was evaluated; the results are in Table 2. The activation energies of PP/PBT blend fibre and PP/PET (OLPET) blend fibre were lower than that of PP/PET (EDSA) blend fibre (Table 2). The results can be proposed that during dyeing process the relaxation of the polymer chains of PP/PBT and PP/PET (OLPET) was less affected by the temperature than in the case of PP/PET (EDSA).

4. Conclusions

In this paper the dyeability of blend PP/PES fibres modified by various PES and compatibilizers as well as the dyeing

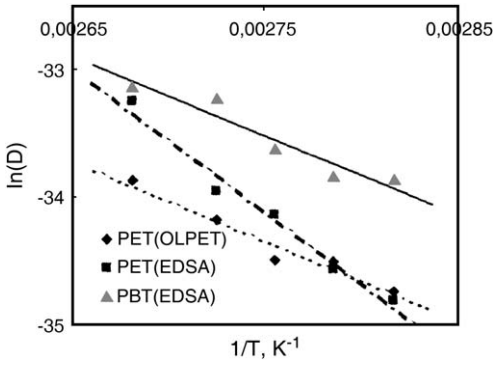

Fig. 2. Relationship between ln D and $1/T$ on activation energy for blend PP/PES fibres.

kinetics were studied. From the obtained results we conclude that:

- The dye uptake of blend PP/PES fibres modified by PET and PBT dyed by disperse dye C. I. Disperse Blue 56 increases with the dyeing temperature and time. The highest dye uptake was measured in blend PP/PES fibres modified by PBT.
- The diffusion coefficients and the dyeing rate constants increase with increase in dyeing temperature. The most significant increase was achieved in blend PP/PES fibres modified by PET (EDSA).
- The blend PP/PET (EDSA) fibre has the highest activation energy in the dyeing by disperse dye C.I. Disperse Blue 56.

Acknowledgements

Support of the National Grant Agency of Slovakia APVT - Grant No 20-010102 and VEGA (Grant FCHFT 926) is appreciated.

References

[1] Prchal V, Marcincin A, Kristofic M, Ondrejmiska K. Dyeing and colourist properties of polypropylene fibres. Vlákna a textile (Fibres and Textiles) 1994;1(3):136–8.
[2] Seves A, Testa G, Marcandalli B, Bergamasco L, Munaretto G, Beltrame PL. Inducing water bath dyeability in polypropylenic fibers by their blending with polyamide 6. Dyes and Pigments 1997;35(4):367–73.
[3] Fan Q, Yang Y, Ugbolue SC, Wilson AR. Dyeable polypropylene via nanotechnology, <http://www.ntcresearch.org/current/year10/Projects/C01-D20.htm>.
[4] Hol. pat. No. 6502104.
[5] Kristofic M. Modified polypropylene fibres. Fibres and Textiles in Eastern Europe 1994;2:38–9.
[6] Marcincin A, Kostialova A, Kristofic M. Textile fibres from polymer blends. Vlákna a textile (Fibres and Textiles) 1998;5(4):210–2.
[7] Prchal V, Kristofic M, Lapcik Jr L, Havlikova B. Colouristic properties of blended PP/PA6 and PP/PET polymer fibres. Fibres and Textiles in Eastern Europe 1997;5:48–50.
[8] Froehling PE, Burkinshaw S. Dendritic polymers: new concept for dyeable polypropylene fibers. In: Man-made fiber year book August 2001. p. 19–20.
[9] Burkinshaw SM, Froehling PE, Mignanelli M. The effect of hyperbranched polymers on the dyeing of polypropylene fibres. Dyes and Pigments 2002;53(3):229–35.
[10] Ruys L. Dyeable PP: a breakthrough in old problems. Chemical Fibres International 1997;47:376–84.
[12] Marcincin A, Brejka O, Murarova A, Hodul P, Brejkova A. Exhaust dyeable polypropylene fibres. Vlákna a textile (Fibres and Textiles) 1999;6(3):119–24.
[16] Ujhelyiova A, Bolhova E. Crystallisation behaviour of polypropylene in blend PP/PET fibres. Vlákna a textile (Fibres and Textiles) 2003;10(4):163–7.
[17] Cegarra J, Puente P. Considerations on the kinetics of the dyeing process of polyester fibers with disperse dyes. Textile Research Journal 1967;37(5):343–50.
[18] Marcinčin A, Ujheliyova A, Marcincinova T. Fibre-forming blends of polypropylene and polyethylene terephthalate. Macromolecular Symposia 2001;176:65–72.
[19] Peters RH. The physical chemistry of dyeing. In: Textile chemistry, vol. III. Elsevier Scientific Publishing Company; 1975. p. 143–180.
[20] Crank J, Park GS. Diffusion in polymers. London, New York: Academic Press; 1968.
[21] Wang PY, Ma JF. The kinetics of the dyeing and fading of coloured poly(ethylene-2,6-naphthalenedicarboxylate) fiber. Dyes and Pigments 1998;37(2):121–7.
[22] Etters JN. Adventures in textile chemistry. Textile Chemist and Colorist 1994;26(12):17–23.
[23] Park KH, Koncar V. Diffusion of disperse dyes into supermicrofibres. AUTEX Research Journal 2004;4(1):45–51.
[24] Kim TK, Son YA, Lim YJ. Thermodynamic parameters of disperse dyeing on several polyester fibres having different molecular structures. Dyes and Pigments 2005;67:229–34.
[25] Alan J. The theory of coloration of textiles. 2nd ed. West Yorkshire: Society of Dyers and Colourists; 1989. p. 396–400.