Dyes and Pigments 94 (2012) 386–392

Contents lists available at SciVerse ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

The kinetic and thermodynamic parameters of dyeing of polypropylene/Clay composite fibers using disperse dye

Navid Rabiei, Mohammad Haghighat Kish, Seyed Hossein Amirshahi*, Maryam Radjabian

Department of Textile Engineering, Amirkabir University of Technology (Tehran Polytechnic), Tehran 15914, Iran

ARTICLE INFO

Article history:
Received 14 December 2011
Received in revised form
12 February 2012
Accepted 15 February 2012
Available online 22 February 2012

Keywords:
PP fiber
PP/Clay composite fiber
Dyeing
Thermodynamic factors
Kinetic factors
Disperse dye

ABSTRACT

The physicochemical parameters of dyeing of PP/Clay composite fiber with disperse dye are investigated in terms of sorption isotherm, standard affinity, enthalpy and entropy changes, diffusion coefficient as well as activation energy of the diffusion. Results are then compared with corresponding properties of the virgin polypropylene fiber. The sorption of disperse dye on PP/Clay composite and polypropylene fiber shows the linear isotherm. The standard affinity of dye to PP/Clay fiber is noticeably higher than that to the virgin polypropylene fiber, while the dyebath containing virgin fiber reveals the higher negative values of the enthalpy and entropy changes than corresponding factors for the dyebath containing composite fiber. For PP/Clay fiber, the value of diffusion coefficient of dye molecules increases with the dyeing temperature. The activation energy of diffusion of dye into the composite fiber is significantly higher than that into the virgin fiber.

1. Introduction

Polypropylene (PP) is a multi-purpose and greatly used man-made polymer in many industrial fields. While the polymer benefits from some remarkable advantages such as low cost, high flexibility, abrasion resistance, light weight, high strength, high toughness and resistance to chemicals, it suffers from some lack of dyeability with classical dyeing methods that are critical in textile application. More specifically, PP fibers are not dyeable because of its non-polar nature, aliphatic structure as well as high crystallinity and high stereo-regularity, which limit the accessibility of dye molecules. These properties of polypropylene have led to, firstly, insufficient chemical affinity between the fibers 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, secondly, the poor accessibility of dyes on the fibers, due to the high degree of crystallinity of polymer [1,2]. However, the dyeability of PP fibers could be improved by chemical and physical modifications of polymer.

Several researchers explored the problem of dyeing PP fibers. The structural modification of PP by chemical reactions and graft copolymerization to yield water-bath dyeable PP fibers [3–5] has been investigated. Besides, blending with other polymers such as polyamide [6–8], poly (ethylene-co-vinyl acetate) [9], polyvinyl alcohol [10], polystyrene [11], polyester [2], hyperbranched polymer [12] and hydrogenated oligocyclopentadiene [13] has been reported. Employing of low temperature plasma technique [14] is also recommended for imparting dyeability to PP fibers.

Despite all valuable attempts made by investigators, it is clear that the major advantage of polypropylene over other polymers such as nylon and polyester is its relatively low price. However, traditional approaches to provide dyeability, such as copolymerization, polyblending, grafting, plasma treatment and specially designed dyes considerably increase the overall cost of fiber manufacturing and/or dyeing procedure. So far, none of these technologies have been welcomed by the manufactures. In fact such modifications cannot produce commercial dyeable polypropylene in fine denier textile fibers for clothing and upholstery, mainly because of higher cost, a decrease of fiber mechanical properties and/or unacceptable dyeability. None of these disadvantages applies to nanoparticles which are affordable and readily available. Moreover, since the nanoparticles can be dispersed into polymer melts like pigments, nanocomposite polypropylene can be spun using current polymerization and extrusion equipment.

---

* Corresponding author. Tel.: +98 21 64542642; fax: +98 21 66400245.
E-mail addresses: seiednavidrabiei@aut.ac.ir (N. Rabiei), mhkish@aut.ac.ir (M.H. Kish), hamirsha@aut.ac.ir, samirshahi@yahoo.com (S.H. Amirshahi), marmar_rajabian@yahoo.com (M. Radjabian).

0143-7208/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2012.02.010

Hence, the application of nanoparticles for improving the dyeing property of polypropylene matrix was recently investigated [10,15–17]. Results showed that the dyeability of filled polypropylene matrix with clay nanoparticles was significantly improved. The quantity and the distribution of clay nanoparticles in the polypropylene matrix have strong effect on the color yield as well as the levelness of dyeing.

However, the improvement in dyeability of PP/Clay nanocomposite was examined by measuring the surface reflectance function of colored samples, i.e. K/S values [10,15–17]. Whereas, the employed function does not seem to be a suitable criterion for analytical evaluation of dyeing systems. In scientific point of view, the K/S is a coarse parameter which does not necessarily reflect the analytical aspects of dyeing system.

Normally, the dyeing process of fibers could be explained through four consistent steps, i.e. migration of dyes from the dyebath toward the surface of fiber, adsorption on the fiber surface, diffusion of dyes into the fiber, and fixation of diffused dyes inside the fiber [2,18]. The diffusion of dye into fiber that is in fact the lowest step of dyeing process depends on several parameters such as type of fibers and dyes, the employed pH, temperature and auxiliaries. In fact, the rate of dyeing is affected by the slowest stage, i.e. the diffusion rate of dye molecules inside the fiber [2,18]. The diffusion of dye molecules into fibers from a well-stirred solution could be expressed by Wilson's equation for finite and by Hill's equation for infinite dyebaths [2].

In the present work, the dyeing mechanism of disperse dye on the polypropylene fibers modified by clay particles is investigated by study of the adsorption and diffusion properties in the infinite dyebath at different temperatures. In fact, some of the physicochemical properties of dyeing such as the equilibrium adsorption isotherm, standard affinity, enthalpy and entropy changes, the diffusion ability parameters (e.g. diffusion coefficient and activation energy of diffusion) and the adsorption rate equation, which have not been reported by other researchers on PP/Clay composite fibers, have been investigated. Eventually, dyeing behavior and mechanism of fixation of disperse dye on PP/Clay composite fibers are compared with virgin PP fibers by correspondent thermodynamic and kinetic parameters.

2. Experimental

2.1. Materials

The fiber grade polypropylene homopolymer, named Moplen HP552R, was purchased from Arak Petrochemical Co. (Arak, Iran), and used as received. The functionalized polypropylene with 0.5 wt.% of maleic anhydride (Polybond 3150) supplied by Chemtura Co. was used as a compatibilizer. The organic modified montmorillonite (OMMT) was Dellite 67G from Laviosa Chimica Mineraria S.P.A. (Livorno, Italy). Polypropylene clay composite was made using a corotative twin-screw extruder (Werner & Pfleiderer, ZSK25). The multi filament yarns from polypropylene clay hybrid were made through a melt spinning process (Fourne Bonn, Germany). In fact, the blending problem between the hydrophilic clay and the hydrophobic non-polar PP was solved by using maleic anhydride-grafted polypropylene copolymer (PP-g-MA) as compatibilizer.

The abbreviated names, the preparation method for PP/Clay hybrid nanocomposite and the amount of OMMT and employed compatibilizer for preparation of different samples are reported in Table 1.

Table 1
Composition of the samples and processing condition.

Sample code	Instrument used	OMMT[a] (wt.%)	PP-g-MA[b] (wt.%)
PP	TSE[c]	0	0
PP/Clay	TSE	1	3

[a] OMMT = organo-modified montmorillonite.

[b] PP-g-MA = maleic anhydride-grafted polypropylene copolymer, polybond 3150, solvay used as compatibilizer.

[c] TSE = twin-screw extruder.

Sample of fibers were scoured by 1 g/l of nonionic surfactant at 80 °C for 20 min with the liquor-to-goods ratio of 40:1 and the procedure was followed by washing in cold distilled water and ambient drying. The selected disperse dye for this work was the commercial grade of C.I. Disperse Blue 56 named Serilene Blue RL without further purification that was purchased from Yorkshire Group, UK. The employed disperse dye belongs to low energy group of disperse dyes [19] and its structure is shown in Table 2.

2.2. Adsorption extent of dye on the fiber

The dye concentration in the bath was measured using Cary 100 UV–vis spectrophotometer. Calibration was obtained with properly diluted stock solutions of dye. To grant the validity of Beer's law, a mixture of 99.6% ethanol and 0.4% distilled water was used as the solvent [20]. The decrease in the total amount of dye in the dyebath was considered as the amount of dye on the fiber. For determination of the kinetic parameters of dyeing, dyestuff was extracted from the dried fibers by using absolute chloroform at room temperature. Again, the concentrations of extracted dye from the samples were determined by the spectrophotometric measurement of solutions.

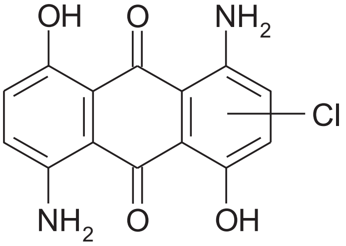
2.3. Dyeing equilibrium parameters

Dye sorption isotherms as well as the commonly used dyeing equilibrium parameters, i.e. standard affinity, enthalpy and entropy changes of dyeing baths were determined for PP/Clay composite and the virgin polypropylene fibers with disperse dye.

2.3.1. Dye sorption isotherm

0.1 g of PP and PP/Clay were individually dyed in the solutions containing 0.01, 0.02, 0.03, 0.04, 0.05 and 0.06 g/l of dye at three different temperatures, 80, 100 and 120 °C, until equilibrium sorption was obtained. In the experiments, the equilibrium was achieved within 2–3 h, depending on temperature and type of sample. However, to assure the achievement of equilibrium, dyeings were prolonged at the desired temperatures for 5 h. To prepare a semi-infinite dyebath, the liquor-to-goods ratio was fixed at 1000:1. Finally, the partition coefficients of dye between the bath (C_b) and the fiber (C_f) in equilibrium were determined at mentioned dyeing temperatures.

Table 2
Chemical structure of Disperse Blue 56.

Serilene Blue RL CI Disperse Blue 56 CI Constitution 63285


2.3.2. *Standard affinity*

Equation (1) shows that the standard affinity ($-\Delta\mu^\circ$) can be calculated by using the partition coefficient (K) that obtained from adsorption isotherm.

$$-\Delta\mu^\circ = RT\ln\left(C_f/C_b\right) = RT\ln K, \tag{1}$$

where, $-\Delta\mu^\circ$ is the affinity of dye molecules to the fiber (cal/mol), R and T are the gas constant (1.9872 cal/mol K) and the absolute temperature (K), respectively. C_b and C_f demonstrate the concentration of dye in the bath (g/l) and the fiber (g/kg fiber) in equilibrium and K is partition coefficient of dyeing reaction.

2.3.3. *Enthalpy change*

According to the Clausius-Clapeyron equation, Eq. (2), the slope of Eq. (3) shows the dyeing enthalpy (ΔH°), and could be simply determined by plot of $-\Delta\mu^\circ/T$ versus $1/T$.

$$\Delta H^\circ = d(\Delta\mu^\circ/T)/d(1/T) \tag{2}$$

$$-\Delta\mu^\circ/T = -\Delta H^\circ/T + C, \tag{3}$$

where, ΔH° and C are the heat of dyeing (cal/mol) and the integration constant, respectively.

2.3.4. *Entropy change*

The entropy change (ΔS°) of dyeing bath was calculated from the experimental plot that shows the relationship between $-\Delta\mu^\circ$ and T as is shown by Eq. (4).

$$-\Delta\mu^\circ = T\Delta S^\circ - \Delta H^\circ \tag{4}$$

2.4. *Dyeing rate parameters*

The rate of sorption of dye by fibers is controlled and studied by several fundamental physicochemical parameters. In this study, the most practical parameters, i.e. dyeing rate constant (k), diffusion coefficient (D) and the activation energy of the diffusion (E) were determined for both types of polypropylene fibers.

2.4.1. *Dyeing rate constant*

To determine the dyeing rates, the fiber samples were dyed in bath containing 0.06 g/l of the dye at the temperatures of boil and 85 °C and the liquor-to-goods ratio of 1000:1. The dyebaths were heated to the dyeing temperature before the fibers were immersed into the dyebath. The Vickerstaff's hyperbolic rate equation, i.e. Eq. (5), was employed to calculate the rate constant of dyeing (k).

$$k\cdot t = (1/(C_\infty - C_t) - (1/C_\infty)), \tag{5}$$

where, C_∞ is the dye uptake (g/kg fiber) at equilibrium, and C_t is the dye uptake (g/kg fiber) at time t.

2.4.2. *Half dyeing time*

The half dyeing time ($t_{1/2}$) was calculated by Eq. (6).

$$t_{1/2} = 0.5C_\infty, \tag{6}$$

where, $t_{1/2}$ shows the half dyeing time in minute.

2.4.3. *Diffusion coefficient*

Different methodologies were suggested to calculate the diffusion coefficient (D) of dye into fiber in dyeing process depending on the employed dyeing procedure and the physical shape of material [2,18,19]. In this work, the Hill's equation was employed to determine the diffusion coefficient of dye into different fibers. According to Hill's equation, the diffusion coefficient was calculated by plotting C_t/C_∞ versus $t^{1/2}$ for the early stage of dyeing, using Eq. (7).

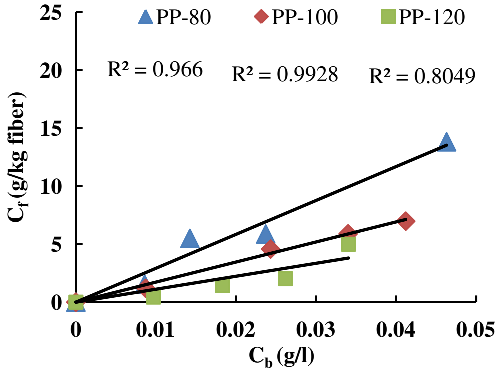


Fig. 1. Sorption isotherms of Disperse Blue 56 on PP at different temperatures.

$$C_t/C_\infty = 4\left(Dt/\pi r^2\right)^{1/2}, \tag{7}$$

where, r is the radius of the cylindrical fiber in centimeter.

2.4.4. *Activation energy of the diffusion*

The activation energy of the diffusion (E) was calculated by Eq. (8).

$$\mathrm{Ln}D_T = \ln D_0 - (E/RT), \tag{8}$$

where, D_T is diffusion coefficient (cm^2/min) at the absolute temperature T (K) and D_0 is constant.

3. Results and discussion

3.1. *Dyeing equilibrium*

3.1.1. *Adsorption isotherms and standard affinity*

The adsorption isotherms of C.I. Disperse Blue 56 on virgin PP and PP/Clay at three different temperatures are respectively shown in Figs. 1and 2. As the figures show, for both types of fibers the linear isotherms (Nernst Isotherm) describe the relationship between sorption extent of the dye on fiber and the amount of the dye in dyebath. The Nernst's adsorption isotherms obtained through sorption of disperse dyes on synthetic fibers can be commonly interpreted as the distribution of dyes in the aqueous phase and the solid solution of the fiber. The well known solid

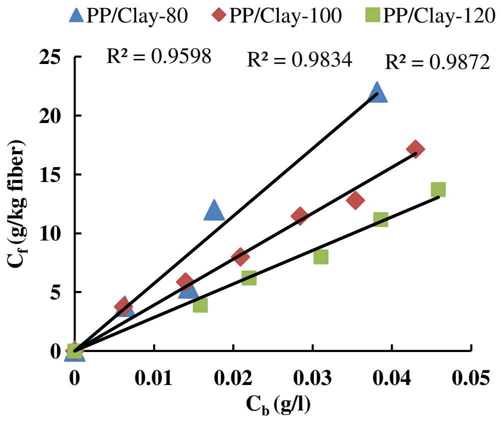


Fig. 2. Sorption isotherm of Disperse Blue 56 on PP/Clay at different temperatures.

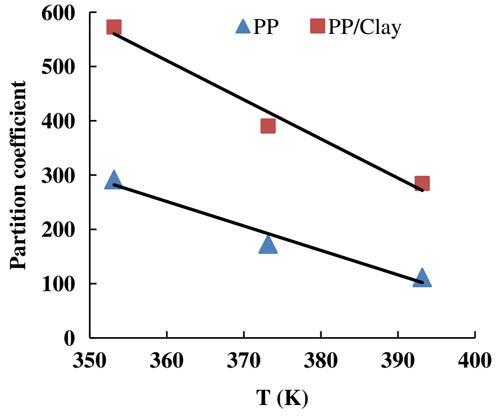


Fig. 3. Partition coefficient against dyeing temperature for PP and PP/Clay.

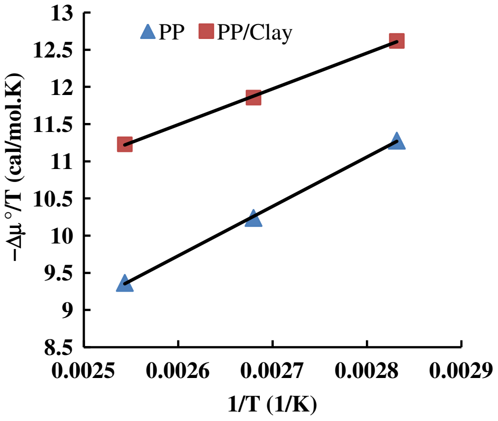


Fig. 4. Plot of $-\Delta\mu^\circ/T$ against inverse of dyeing temperature ($1/T$) for computation of enthalpy change.

solution theory which is accepted for the interaction of disperse dyes with the synthetic fibers could be simulated by the distribution of a solute in tow immiscible solvent in a mixture.

As shown in Fig. 3, the partition coefficient (K) is affected by the dyeing temperature. As the temperature increases, the partition coefficient of dye decreases for both fibers. Since the adsorption of dyes on fiber is an exothermic reaction process, the thermodynamic adsorption or the partition coefficient can be negatively affected by using the higher dyeing temperature. Fig. 3 also shows an interesting phenomenon that is the different effect of temperature on partition coefficient of dye for PP/Clay in comparison with virgin polypropylene fibers. As the figure shows, the rate is significantly greater for PP/Clay than that for the PP fibers. The differences originate from the different morphological properties of fibers and their interactions with dye molecules.

The differences between the driving forces of dye molecules to polypropylene and the modified fibers were studied by determination of the standard affinities of dye to both fibers. Equation (1) was used to calculate the value of affinity. By using the isotherm data, K, at three different temperatures, the corresponding values of standard affinities of dye for both fibers were calculated and shown in Table 3.

As Table 3 shows, the standard affinity decreases with increasing of temperature for both fibers. As one expects from an exothermic reaction, the higher dyeing temperature leads to a negative effect on the thermodynamic adsorption [21]. Totally, the standard affinities of dye to PP/Clay are considerably higher than those to virgin PP. This finding reveals that the tendency of dye molecule for moving from its standard state in the dyebath to its standard state in the PP/Clay fiber is significantly higher than that to its standard state in PP.

3.1.2. Enthalpy and entropy changes

The adsorption of dye on fibers is an exothermic process and releases heat energy [21,22]. Obviously, the dyeing conditions, such as types of fibers, dyes and the dyeing media affect the amount of released heat of dyeing. In fact, the enthalpy change in the dyeing system shows the amount of exothermic energy arising out of interaction between the polymeric chains of fiber and dye. Consequently, the enthalpy change is primarily considered as the measure of the adsorption strength of dyes. Fig. 4 demonstrates the linear relationship between $-\Delta\mu^\circ/T$ and $1/T$ on enthalpy change (ΔH°) as shown in Eq. (3). The enthalpy changes for both fibers are summarized in Table 4. According to this table, the enthalpy change of dyebath containing PP/Clay is lower than that of dyebath containing PP; i.e. the amount of the released thermal energy when dye molecules are absorbed into polymeric matrix in PP/Clay was lower than that in PP. So, it could be concluded that the dye molecules in PP are more strongly embedded within the polymer molecules than PP/Clay.

Table 3
The partition coefficient (K) and the standard affinity ($-\Delta\mu^\circ$) of C.I. Disperse Blue 56 on PP and PP/Clay.

Temperature (°C)	PP		PP/Clay	
	K	$-\Delta\mu^\circ$ (cal/mol)	K	$-\Delta\mu^\circ$ (cal/mol)
80	291.68	3982.66	572.75	4456.17
100	172.9	3820.47	390.33	4424.22
120	111.39	3681.77	284.54	4414.40

The PP fiber has not any functional group to hold the dye molecules. Nevertheless, the amount of released thermal energy, due mainly to the presence of weak Van der Waals' forces established during dyeing process, is significantly larger (6643 cal/mol) than that of PP/Clay (4828.6 cal/mol). This explanation and the shape of sorption isotherm suggest that the sorption of dye for PP/Clay fiber does not occur in finite number of identical sites. However, the adsorption of dyes in a non-dissociated form or a mechanism of creating aggregates of dye on fiber seems to be probable [23]. Therefore, the main source of affinity of dyeing or the interactions operating in bonding of dye on fiber can be dissolving of dyes in fiber's bulk via Van der Waals' forces and hydrophobic interactions and consequent aggregation of dyes in fiber [24].

According to Eq. (4), the overall value of affinity is the sum of the enthalpic and the entropic gains which they are antagonistic. In fact, the entropy change of dyebath implies the entropy difference between the dye molecules within the fiber and dyeing solution. In most dyeing processes, since the adsorbed dye molecules within fiber are more restrained than dyeing solution, the entropy change is negative. Nonetheless, the enthalpy gain is dominant; therefore the dyeing process is commonly described as an enthalpy-driven process.

As Fig. 5 demonstrates, the linear relationship between $-\Delta\mu^\circ$ and T on virgin PP and PP/Clay is evident and according to Table 4,

Table 4
The enthalpy change (ΔH°) and the entropy change (ΔS°) of C.I. Disperse Blue 56 on PP and PP/Clay.

Parameters	PP	PP/Clay
ΔH° (cal/mol)	−6643	−4828.6
ΔS° (cal/mol K)	−7.52	−1.04

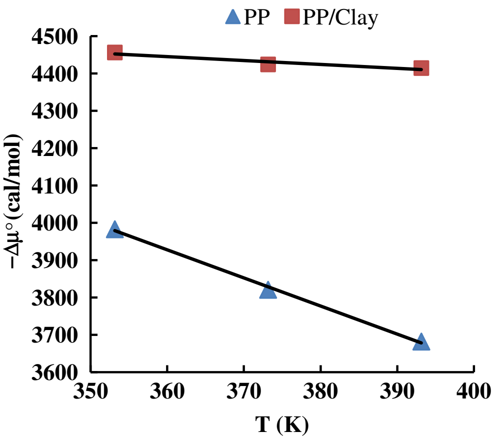


Fig. 5. Plot of standard affinity against dyeing temperature for determination of entropy change.

the entropy change of PP/Clay is lower negative value than PP's. It means that the dye molecules were embedded less compactly in the PP/Clay fiber than PP fiber. In fact, the negatively larger value of entropy change of PP indicates that after completion of dyeing, the mobility and freedom of dye molecules is appreciably reduced for the PP substrate that is in agreement with the literatures [21,22]. It can be attributed to the creation of suitable voids within the PP/Clay fiber. The voids have been formed due to incorporating of clay into the PP matrix. The suggested structure was approved by the crystallinity of fibers. In fact, the crystallinity of PP/Clay is found to be lower than the crystallinity of PP and the subject was studied and claimed that the oriented nanoclay layers provide the tortuous pathways [17]. Thus, it seems more reasonable that the created tortuous pathways can contribute to form the available spaces within PP/Clay fiber to hold and confine dye molecules.

From the chemical structure point of view, since the clay layers in PP/Clay are hydrophilic substances [25], the interaction between hydrophobic disperse dyes and clays in the modified fibers could not be a reasonable interoperation in comparison with possible interaction between the hydrophobic polypropylene chains and the hydrophobic disperse dyes. The facts justify the reasons that PP/Clay has lower negative value of enthalpy and entropy change than those of virgin PP.

3.2. Rate of dyeing

3.2.1. Dyeing rate constant and half dyeing time

In order to compare the dyeing rate of the dye on PP and PP/Clay fibers, the dyeing rate was obtained at 85 °C and boiling temperatures. Fig. 6 demonstrates the two typical rates of dyeing for PP and PP/Clay fibers at boil. The dyeing rate constant (k) was calculated by means of least squares fit of experimental data using Eq. (5) at two different temperatures. The dyeing rate constants and half dyeing time of C.I. Disperse Blue 56 on PP and PP/Clay fibers at two different temperatures are summarized in Table 5. The results also indicate that the half dyeing time of PP/Clay was significantly lower than that of PP at boil.

Table 5
The dyeing rate constant (k) and half dyeing time of C.I. Disperse Blue 56 on PP and PP/Clay.

Temperature (°C)	PP		PP/Clay	
	k (min^{-1})	$t_{1/2}$ (min)	k (min^{-1})	$t_{1/2}$ (min)
Boil	0.009	11.05	0.009	2.63
85	0.024	8.08	0.002	16.63

As expected, the highest rate constant is accompanied with the lowest half dyeing time for both fibers. However, the highest rate constant for virgin PP is occurred at 85 °C; whereas for the PP/Clay is at boil, and the rate of dyeing for the PP/Clay fibers is strongly related to the temperature of dyeing.

3.2.2. Diffusion coefficient and activation energy of diffusion

As indicated in the literature [19], the D/r^2 was practically calculated to describe the diffusion of dyes into the fiber. By using Eq. (7) for the early stage of dyeing, the C_t/C_∞ should be linearly proportional to the $t^{1/2}$ and the diffusion coefficient (D/r^2) could be obtained from the slop of this equation [19,26]. Fig. 7 shows the relationship between C_t/C_∞ and $t^{1/2}$ on virgin PP and PP/Clay at 85 °C. The values of the diffusion coefficient (D/r^2) of the disperse dye on PP and PP/Clay fibers at three different temperatures are also reported in Table 6.

According to Table 6, the diffusion coefficient of dye into PP/Clay is higher than the diffusion coefficient of dye into virgin PP for boiling and 85 °C temperatures while the coefficient is lower for 60 °C. For PP/Clay, as the temperature of dyeing increases, the diffusion coefficient also increases; whereas for virgin PP, the diffusion coefficient of dye decreases with increasing of temperature. Due to the fact that the method of calculation of the diffusion coefficient of dye into fiber is strongly related to the amount of dye uptake, which is time-dependant, by fiber in the initial stage of dyeing, it seems acceptable that the ability of fiber to hold and gain dye molecules in the early stage of dyeing plays a crucial, final role in the value of this kinetic parameter.

According to Hill's equation, the quantity of (C_t/C_∞) is proportional to (Dt/r^2). In fact, the determined diffusion coefficient (D/r^2) has an apparent meaning because the sum of the adsorbed dye by the fiber at a certain time of dyeing represents an integral of concentration profiles. For each period of time (0–3, 0–6, 0–12, 0–24 and 0–36), when the temperature increases (from 60 °C to

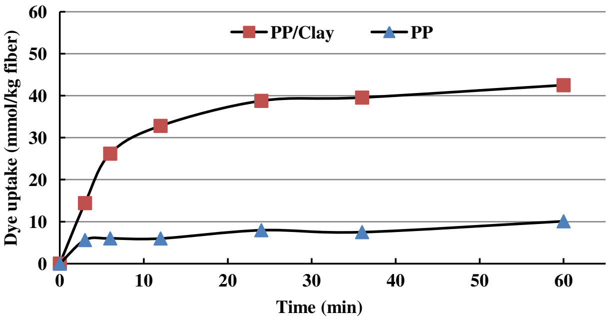


Fig. 6. The rate of dye uptake against dyeing time for PP and PP/Clay at boil.

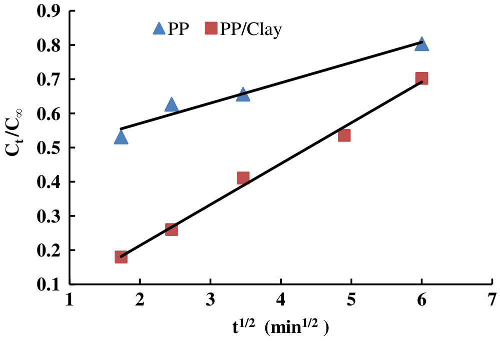


Fig. 7. Variation of C_t/C_∞ against $t^{1/2}$ for determination of diffusion coefficient.

Table 6
The diffusion coefficient (D) of C.I. Disperse Blue 56 on PP and PP/Clay.

Temperature (°C)	$D/r^2 \times 1000$ (min^{-1})	
	PP	PP/Clay
Boil	0.549	5.674
85	0.692	2.813
60	3.137	1.813

boil), the amount of (C_t/C_∞) increases as well. For example at the temperature 60 °C, (C_{0-6}/C_∞) is larger than (C_{0-3}/C_∞) or (C_{0-24}/C_∞) is larger than (C_{0-12}/C_∞). The rate of changes of (C_t/C_∞) with different time durations, however, decreases with increasing of temperature. For instance, at 60 °C, the value of $((C_{0-6}/C_\infty)-(C_{0-3}/C_\infty))$ is larger than the value of $((C_{0-6}/C_\infty)-(C_{0-3}/C_\infty))$ at 85 °C or boil. Similarly, the value of $((C_{0-12}/C_\infty)-(C_{0-6}/C_\infty))$ at 60 °C is larger than the value of $((C_{0-12}/C_\infty)-(C_{0-6}/C_\infty))$ at 85 °C or boil. It seems that the reason for this type of behavior originates from the capability of PP to hold dye molecules within its polymeric matrix. The capability of retaining dye molecules by PP at lower temperatures is greater than that at higher temperatures. In fact, when the temperature increases, the level of kinetic energy of dye molecules also increases that could lead to desorption of dye molecules because of the lack of suitable sites and/or positions to hold dye molecules within the polymeric matrix. Therefore, the rate of desorption of dye molecules from PP matrix at higher temperature is faster than that at lower temperatures. Since this rate determines the value of dye diffusion coefficient into PP, the parameter decreases at higher temperature and resulting in negative activation energy.

The pronounced difference between the value of diffusion coefficient of dye into PP and PP/Clay at higher temperatures can be explained by the hydrophilic behavior of clay layers [25]. In fact, the hydrophilic characteristic of clay increases the hydrophilicity of PP/Clay substrate leading to increase the swelling property of PP/Clay than that of PP. In other words, the internal structure of virgin PP substrate during the dyeing process is more rigid than that of PP/Clay that could lead to less penetration in comparison with PP/Clay fibers. Besides, at the higher temperatures, the free volume in the PP/Clay fibers would be higher that could lead to higher diffusion coefficient in comparison with virgin PP.

It is no doubt that the crystallinity plays an important role in this issue and the higher degree of crystallinity of virgin PP in comparison with PP/Clay fibers reconfirms the findings [17]. Clearly, the small decrease in the crystallinity (lower than 5%) could not be solely responsible for the higher dyeability of PP/Clay fibers [17]. Moreover, in the case of PP/Clay, the accessibility of the fiber can be improved by incorporation of particles that create pathways in the polymer structure. Such pathways make the penetration of dye molecules toward the internal spaces of fibers more possible.

The activation energy of the diffusion was calculated by the well known Arrhenius equation shown by Eq. (8) and the results are demonstrated in Table 7. Fig. 8 shows the linear relationship between the Ln (D_T/r^2) and $1/T$ for both fibers. The activation energy of the diffusion (E) explains the dependence of diffusion coefficient on the dyeing temperature and also represents the energy barrier that a dye molecule should overcome to diffuse into the polymer chains [22,27].

Table 7
The activation energy of the diffusion (E) for C.I. Disperse Blue 56 on PP and PP/Clay.

Parameter	PP	PP/Clay
E (cal/mol)	−12025	6958

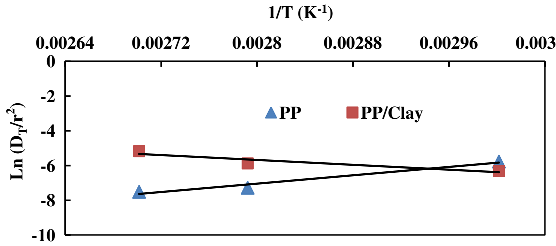


Fig. 8. Plot of Ln (D_T/r^2) against $1/T$ for determination of activation energy.

The negative value of the activation energy of diffusion in PP is shown in Table 7. The result can be explained by kinetic energy of dye molecules to diffuse into polymeric matrix of PP. Indeed, the level of kinetic energy of dye molecules at low temperatures, e.g. 60 °C, to diffuse into virgin PP is sufficient. Due to increasing in the level of kinetic energy of adsorbed dye molecules inside the fiber, as the temperature increases, desorption of dye molecules is occurred. In other words, as the temperature increases the value of diffusion coefficient which is related to the value of (C_t/C_∞) decreases. Therefore, the negative value for this parameter was obtained because the diffusion rate decreased as the temperature was raised. Indeed, this behavior simply means that the reverse reaction process (corresponding to desorption of dye molecules from PP) is so sensitive to temperature than direct reaction, i.e. dye adsorption. Consequently, the rate increases sharply as the temperature is raised, and depletes the steady-state concentration [28]. This unusual and unexpected behavior of virgin PP probably arises from the lack of sites to hold high kinetic energy level dye molecules within polymeric matrix that could be reconfirmed by the poor interactions between the dye molecules and the polymeric chains of PP.

In the case of PP/Clay, however, at lower dyeing temperatures, dye molecules benefit from low kinetic energy for diffusion into PP/Clay, and therefore they penetrate more slowly into the fiber. Thus, as temperature increases, the diffusion coefficient also increases, i.e. a good correlation is established between diffusion coefficient and the dyeing rate constant. In fact, the higher diffusion coefficient of dye and the dyeing rate constant indicate that the dyeing rate is probably controlled by the diffusion of dye into the PP/Clay fiber.

Finally, the higher dyeability of PP/Clay polymer could be concluded from the fact that the dyeing behavior of a fiber depends on both its physical and chemical structure. From the chemical structure point of view, dyeability is governed by the presence, firstly, of polar groups which interact with water molecules and allow fiber swelling and, secondly, by the functional groups which could attract the dye molecules [17,29]. For PP, the non-polar nature and the lack of functional group to hold dye molecules cause serious limitations in dyeing. Because of the hydrophilic nature of clay particles, incorporating clay particles allows fiber swelling and creates pathways to form some voids inside the polymeric matrix of fiber to hold dye molecules physically. From the physical structure point of view, the fiber must be accessible to water, dyes and other reagents. It must have a certain permeability, particularly to permit the dye molecules to diffuse into the fiber matrix [17,29].

4. Conclusion

Thermodynamic and kinetic parameters of dyeing of incorporated PP with clay particles were deeply investigated and compared with those of the virgin PP. The parameters were discussed in terms of the relationship between the internal structure of fibers and the dye adsorption. The standard affinity of dye to PP/Clay was significantly higher than that to PP. On the other hand, the higher negative values of enthalpy and entropy changes for virgin PP were found. For the PP/Clay fibers, as the temperature increased, the diffusion coefficient also increased. The activation energy of PP/Clay fibers was higher than that of PP. In respect of dyeing mechanism, while the dyeing sites are not available for both types of fibers, the clay particles provide a type voids that could keep the dye molecules. In addition, clay particles improve the accessibility of the fiber sites, which is very important for effective dyeing procedure.

Acknowledgment

The authors would like to thank Dr Samira Aslanzadeh for providing the PP and PP/Clay filaments for this research.

References

[1] Ahmed M. Polypropylene fibers-science and technology. New York: Elsevier; 1982.

[2] Ujhelyiova A, Bolhova E, Oravkinova J, Tiňo R, Marcinčin A. Kinetics of dyeing process of blend polypropylene/polyester fibers with disperse dye. Dyes Pigm 2007;72:212–6.

[3] Tehrani BAR, Shoushtari AM, Malek RMA, Abdous M. Effect of chemical oxidation treatment on dyeability of polypropylene. Dyes Pigm 2004;63:95–100.

[4] Dayloglu H. Polymeric dye receptors for disperse dyeable polypropylene fibers. J Appl Polym Sci 1992;46:1539–45.

[5] Samanta AK, Sharma DN. Dyeing of polypropylene with some azo disperse dye of basic character via chlorination route. Ind J Fib Tex Res 1995;20:206–10.

[6] Asiaban S, Moradian S. Investigation of tensile properties and dyeing behavior of various polypropylene/polyamide 6 blends using a mixture experimental design. Dyes Pigm 2012;92:642–53.

[7] Seves A, Testa G, Marcandalli B, Bergamasco L, Munarretto G, Beltrame PL. Inducing water bath dyeability in polypropylenic fibers by their blending with polyamide 6. Dyes Pigm 1997;35:367–73.

[8] Kotek R, Afshari M, Gupta BS, Kish MH, Jung D. Polypropylene alloy filaments dyeable with disperse dyes. Color Technol 2004;120:26–9.

[9] Son TW, Lim SK, Chang CM, Kim SS, Cho IS. Physical modification of polypropylene: preparation of fibers with disperse dyes. J Soc Dye Col 1999;115:366–9.

[10] Ujhelyiová A, Srecká Z, Bolhová E, Dulíkova M, Bugaj P. Polypropylene fibers modified by polyvinyl alcohol and nanoadditive: structure and properties. Fibers Text East Eur 2007;15:37–40.

[11] Sengupta AK, Sen K, Mukhopadhydy A. False twist texturization of polypropylene multifilament yarns. Part IV: structural influences on dye uptake. Text Res J 1986;56:511–5.

[12] Burkinshaw SM, Froehling PE, Mignanelli M. The effect of hyperbranched polymers on the dyeing of polypropylene fibers. Dyes Pigm 2002;53:229–35.

[13] Seves A, Macro T, Siciliano A. Blending polypropylene with hydrogenated oligocyclopentadiene: a new method for the production of dyeable fibers. Dyes Pigm 1995;28:19–29.

[14] Rashidi A, Moussavi PH, Mirjalili M, Ghoranneviss M. Application of low temperature plasma on modification of polypropylene. J Plasma Fusion Res 2002;5:255–60.

[15] Toshniwal L, Fan Q, Ugbolue SC. Dyeable polypropylene fibers via nanotechnology. J Appl Polym Sci 2007;106:706–11.

[16] Effenberger F, Schweizer M, Mohamed WS. Effect of montmorillonite clay nanoparticles on the properties of polypropylene fibers. Polym Plast Technol Eng 2010;49:525–30.

[17] Razafimahefa L, Chelebicki S, Vroman I, Devaux E. Effect of nanoclay on the dyeability of polypropylene nanocomposite fibers. Color Technol 2008;124:86–91.

[18] Ahmadi Shoar J, Amirshahi SH, Malek RMA. Trial the microscopic images for determination of diffusion behavior of dyes in fibrous material. J Appl Polym Sci 2009;112:1030–6.

[19] Yang Y, Brown H, Shiqi L. Some sorption characteristics of poly(trimethylene terphethalate) with disperse dyes. J Appl Polym Sci 2002;86:223–9.

[20] Golob V, Tusek L. VIS absorption spectrophotometry of disperse dyes. Dyes Pigm 1999;40:211–7.

[21] Trotman ER. Dyeing and chemical technology of textile fibers. 6th ed. New York: John Wiley and Sons, Inc.; 1984.

[22] Kim TK, Son YA, Lim YJ. Thermodynamic parameters of disperse dyeing on several polyester fibers having different molecular structures. Dyes Pigm 2005;67:229–34.

[23] Akrman J, Prikryl J. Dyeing behavior of polypropylene blend fiber. 1. Kinetic and thermodynamic parameters of the dyeing system. J Appl Polym Sci 1996;62:235–45.

[24] Razafimahefa L, Vroman I, Viallier P. Mechanisms of fixation of dyestuffs in polyamide 6.6 fibers. Color Technol 2003;119:10–3.

[25] Ladhari A, Daly HB, Belhadjsalah H, Cole KC, Denault J. Investigation of water absorption in clay-reinforced polypropylene nanocomposites. Polym Degrad Stabil 2010;95:429–39.

[26] Crank J. Mathematics of diffusion. 2nd ed. London: Oxford University Press; 1975.

[27] Alan J. The theory of coloration of textiles. 2nd ed. West Yorkshire: Society of Dyers and Colorists; 1989.

[28] Atkins P, Paula DJ. Atkins' physical chemistry. 8th ed. Italy: Oxford University Press; 2006.

[29] Bird CL, Boston WS. Theory of coloration of textiles. Bradford: SDC; 1975.