



Kinetic of Disperse Dyeing on Compounded PET (Polyethylene Terephthalate) Using Hyperbranched Polymeric Additive as a Nanomaterial

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ABSTRACT

This paper presents the influence of Hybrane H 1500 as a hyperbranched polymer on kinetic parameters of dyeing compounded fiber grade PET (polyethylene terephthalate) at boiling temperature. C.I. Disperse Red 324 was used as a disperse dye for dyeing compounded fiber grade PET. The result was compared with corresponding properties of unmodified PET. The dyeing rate constants and diffusion coefficients as the dyeing kinetic parameters were determined. The obtained results indicated that the rate of dyeing is closely related to the diffusion behavior of dye into the fiber. The dyeing rate of modified PET was faster than unmodified PET. It was also found that the modified PET containing 0.5% hyperbranched polymer as an additive had higher diffusion coefficient as well as dyeing rate constant comparing to unmodified PET. Small angle x-ray scattering (SAXS) was used to characterize compounded PET. SAXS measurement determined the size, shape and showed a homogeneous dispersion of hyperbranched polymer in compounded sample. Prog. Color Colorants Coat. 5(2012), 117-124. © Institute for Color Science and Technology.

1. Introduction

PET (Polyethylene Terephthalate) or polyester is the most widely used synthetic fiber in textile industry due to its good physical and chemical properties. In spite of the fact that PET benefits from some advantages, it suffers from low rate of dyeing in conventional dyeing systems because of its rigid structure, high crystallinity and lack

of reactive dye sites. Polyester fibers are dyed with disperse dyes while dyeing is carried out at boiling temperature using carriers or at high temperature without any carrier. Carriers provide not only toxic and hazard influences to the environments but also they usually reduce the light fastness of dyed fiber [1]. For this

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reason, attempts have been done to eliminate carriers during dyeing of polyester fibers.

A large number of researches have been done to improve the dyeability of PET fibers at boiling temperature without using carriers. For example, Raslan et al., worked on modification of polyester fabric using chemical/thermal treatment to improve dyeability. The dyeability of treated fabric with disperse dye was found to be better than untreated one at boiling temperature without using carriers [2]. Another approach has been introduced by Saus et al., in 1993. They applied a new method for dyeing of polyester fibers in which supercritical carbon dioxide (SCD) was used as a transfer medium [3]. Before using the mentioned method, the common dyeing in textile industry used large amounts of water in dyeing processes and emitted dangerous organic compounds such as carriers into the environment. Dyeing polyester fibers in supercritical carbon dioxide instead of water can save energy, reduce water usage and prevent pollution. The PET fibers dyed in supercritical carbon dioxide had good fastness as well as good physical properties [4]. Khatibzadeh et al., used a hyperbranched polymer to improve the dyeability of fiber grade PET in absence of carrier at boiling temperature [5].

The dendritic polymers are divided into two different classes: the monodisperse dendrimers and the polydisperse hyperbranched polymers. Hyperbranched polymers have densely branched structures and a large number of reactive groups. These polymers have successfully been used in various applications, due to their unique physical and chemical properties. They have cavities in their molecule which enable them to trap guest molecules by specific interactions. Furthermore, the low melt viscosity of hyperbranched polymers offers applications as melt modifiers or blend components [6-8]. Using mentioned procedure [5], modified fiber grade PET with a polyesteramide hyperbranched polymer could be dyed at boiling temperature in absence of carriers. However, the improvement in dyeability of PET using hyperbranched polymer was studied by measuring the surface reflectance function of colored samples, i.e. K/S values. Whereas, the employed function does not seem to be a suitable criterion for analytical evaluation of dyeing systems. From scientific point of view, the K/S is a coarse parameter which does not necessarily reflect the analytical aspects of dyeing system [9]. The most widely used equation in general studies of the dyeing process is the homogeneous reaction of the 2nd order, proposed by Vicherstaff [10]. Dyeing kinetic parameters generally

provide accurate information on the rate of dyeing. For this reason, we have undertaken a study on the dyeing kinetic of C.I. Disperse Red 324 on modified PET with a hyperbranched polymer. In this paper, in order to investigate the rate of dyeing of modified PET, diffusion coefficient and rate of dyeing constant are measured as the dyeing kinetic parameters. We also reported small angle x-ray scattering (SAXS) measurement for compounded PET that has been considered to determine the size, shape and dispersion of hyperbranched polymer.

1.1. SAXS theory

According to the SAXS theory, the SAXS signal is produced by electron density inhomogeneity in the sample. In fact, SAXS works on the basis of electronic density difference in the sample. On this basis, x-ray beam passing through the sample scatters in small angles. The angle between transmitted beam and scattered beam is called scattering angle [11].

The scattering intensity is proportional to the square of the density differences between the constituting phases. By plotting scattering intensity vs. scattering vector in logarithmic scale, two regions are achieved. Very small angles are Guinier region and follows Eq. (1):

$$I(q) \propto G \exp\left(-q^2 R_g^2 / 3\right) \quad (1)$$

where $I(q)$ is the scattering intensity, R_g is the gyration radius which indicates a measure of the mean square distance of the scattering centers within particle domains from the center of gravity and q , the scattering vector is defined as Eq. (2):

$$q = \frac{4\pi}{\lambda} \sin\left(\frac{\theta}{2}\right) \quad (2)$$

where λ is the x-ray wavelength and θ is the scattering angle. The R_g is related to the size of particle, and could be calculated from the slope in the linear region of a plot of $\ln(I(q))$ versus q^2 .

A log-log plot of SAXS data, called Porod plot, comforted in other region and could give an indication of the fractal nature of particle, specifically if the system displays a mass or surface fractal behavior [11]. Porod

formula was shown in Eq. (3):

$$I(q) \propto q^{-D} \quad (3)$$

where D is the power law exponent obtained from the slope in the linear region of a double logarithmic plot of $I(q)$ versus q . For $1 < D < 3$ objects are considered as mass fractal in three-dimension with fractal dimension while for $3 < D < 4$ objects are surface fractal with fractal dimension [12].

2. Experimental

2.1. Materials

Fiber grade PET chips (Zimmer Specification, Germany) were provided by Shahid Tondgoyan Petrochemical Company in Iran, with melting point equal to $250 \pm 2^\circ\text{C}$ and T_g about to 80°C .

Hybrane H1500, a dendritic polymer, was kindly provided by DSM from Netherland. Its molecular formula and weight are $(\text{C}_6\text{H}_{15}\text{NO}_2 \cdot \text{C}_8\text{H}_{10}\text{O}_3)_x$ and 1500 g/mol, respectively.

The dyeing of all the fibers were carried out using C.I. Disperse Red 324 (Terasil Red R), a commercial disperse dye which was provided from Ciba company in Iran and was directly used as received without further purification. The employed disperse dye belongs to medium energy group of disperse dyes. This dye is a monoazo dye and its chemical structure is shown in Figure 1.

The maximum absorption wavelength of mentioned disperse dye was measured using a UV-Visible spectrophotometer (Color-Eye 7000A).

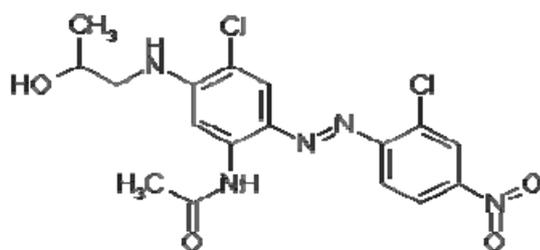


Figure 1: The chemical structure of C.I. Disperse Red 324.

The absorption spectra of the stock solution (0.1mg/mL) C.I. Disperse Red 324 showed that the maximum absorption wavelength was 500 nm. To yield the calibration curve, suitable dilutions of 0.1 mg.mL⁻¹ stock dye solution were prepared and their absorbance was measured at λ_{max} .

2.2. Preparation of sample

An internal mixer (Brabender Plasticorder W50, Brabender Company, Germany) was used to prepare two melted samples including unmodified PET and PET plus 0.5% Hybrane H1500 as a hyperbranched polymer. Then, laboratory mixing extruder (LME) was used to provide fibers from mentioned samples. Samples of fibers were scoured by 2 g/l of nonionic surfactant at 60°C for 30 minutes with the liquor-to-goods ratio of 500:1 and the procedure was followed by washing in cold water and ambient drying.

2.3. Characterization of sample

Small angle x-ray scattering (SAXS) studies were carried out using a S3-MICRO diffractometer (Hecus, Austria) equipped with $\text{CuK}\alpha$ radiation source ($\lambda = 0.154 \text{ nm}$) operating at 40 kV and 49 mA. The data were recorded in the reflection mode over a 2θ range of $\sim 0-10^\circ$ at a rate of $0.04^\circ/\text{min}$.

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) and diffusion coefficient (D) were determined for unmodified and compounded PET fibers.

2.4.1. Dyeing rate constant

For dyeing in this section, 1% of the dye OWF (On Weight of Fibers) was used while the liquor-to-goods ratio was 1000:1. The acidity of the dyebath was adjusted to pH 4.5 using acetic acid. To study the dyeing rate, each dyeing was carried out in a 100 milliliter volume stainless steel daybath using a dyeing machine at boiling temperature followed by various time intervals (1, 3, 5, 10, 20, 30, 60, 90 and 120 min). The dyebaths were heated to the dyeing temperature before the samples were immersed into the dyebath. Then, the dyed samples were removed from the dyebath immediately after each time interval. After dyeing, the dye absorbed on the sample

was obtained by extracting the absorbed dye with N,N-dimethylformamide (DMF) and the dye concentration of the DMF solutions was measured using a spectrophotometer at 500 nm for C.I. Disperse Red 324. Therefore, the adsorbed dye concentration (C_t) at time t was determined. This value was converted to milligrams of dye per gram fiber. The Vickerstaff's hyperbolic rate equation, i.e. Eq. (4), was employed to calculate the dyeing rate constant (k).

$$k.t = (1 / (C_\infty - C_t) - (1 / C_\infty)) \quad (4)$$

where, t is time (min), C_∞ is the dye uptake (mg/g fiber) at equilibrium which for the present study is taken as the dye uptake after 300 minutes, and C_t is the dye uptake (mg/g fiber) at time t .

2.4.2. Diffusion coefficient

Different methods were suggested to obtain the diffusion coefficient (D) of dye into fiber in dyeing process depending on the employed dyeing procedure and the physical shape of material [9]. In this study, the Hill's equation was employed to determine the diffusion coefficient of dye into 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. (5).

$$C_t/C_\infty = 4 (Dt / \pi r^2)^{1/2} \quad (5)$$

where, D is the diffusion coefficient (mm^2/min) and r is the radius of the cylindrical fiber (mm).

3. Results and discussion

3.1. SAXS

In order to study the dispersion of compounded PET with nanostructured hyperbranched polymer, small angle x-ray scattering (SAXS) was used. SAXS profile of unmodified PET exhibited a very low scattering intensity and this means that no particles exist in unmodified PET fiber. The Guinier plot and Porod plot of SAXS data for the compounded PET fiber showed a linear region (Figures 2 and 3).

The R_g and D obtained from the slope of the curves. The power law exponent (D) and R_g for the compounded PET fiber were 2.48 and 12.6 nm, respectively. The power law exponent for the sample was lower than 3, suggesting that compounded PET fiber had mass fractal behavior [12]. So based on this result, the shape of hyperbranched polymer can be imagined to is similar to Figure 4.

3.2. Kinetics

In order to compare the dyeing rate of the C.I. Disperse Red 324 on both unmodified and modified PET fibers, the dyeing rate was obtained at boiling temperature.

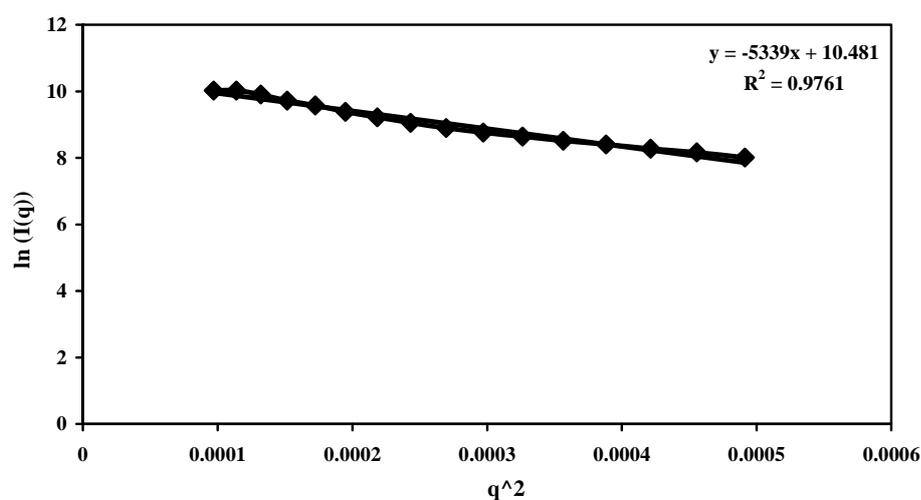


Figure 2: Guinier plot of SAXS for compounded PET with hyperbranched polymer.

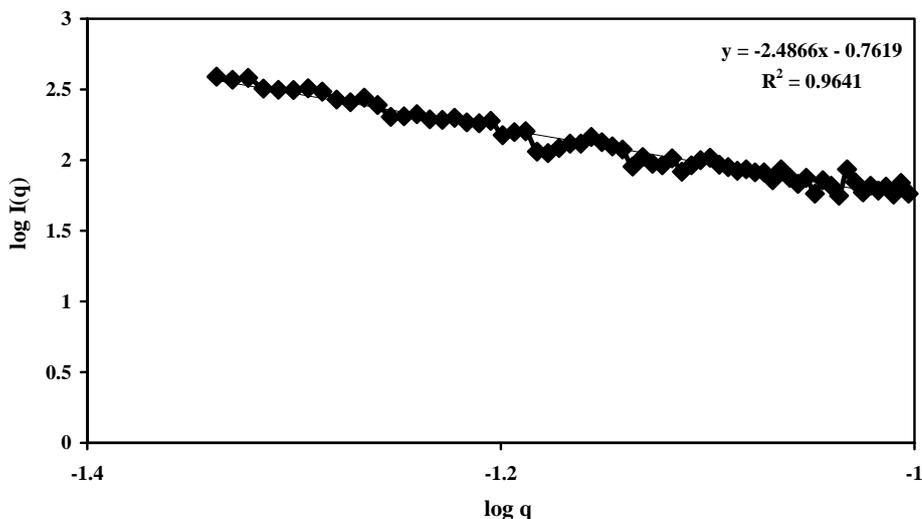


Figure 3: Porod plot of SAXS for compounded PET with hyperbranched polymer.



Figure 4: The schematic shape of hyperbranched polymer.

Table 1: Dyeing rate constants (k) and diffusion coefficients (D/r^2) for unmodified and modified PET fibers at boiling temperature.

Fiber	k (mg/g.min ^{1/2})	D/r^2 (mm ² /min)
PET	0.08	0.87×10^{-5}
PET + 0.5%H	0.12	1.35×10^{-5}

Figure 5 demonstrates the two rate of dyeing curves for unmodified and modified PET fibers at boiling temperature. The dyeing rate constant (k) was calculated by means of least squares fit of experimental

data using Eq. (4) at boiling temperature. The dyeing rate constants of C.I. Disperse Red 324 for both fibers at boiling temperature are given in Table 1.

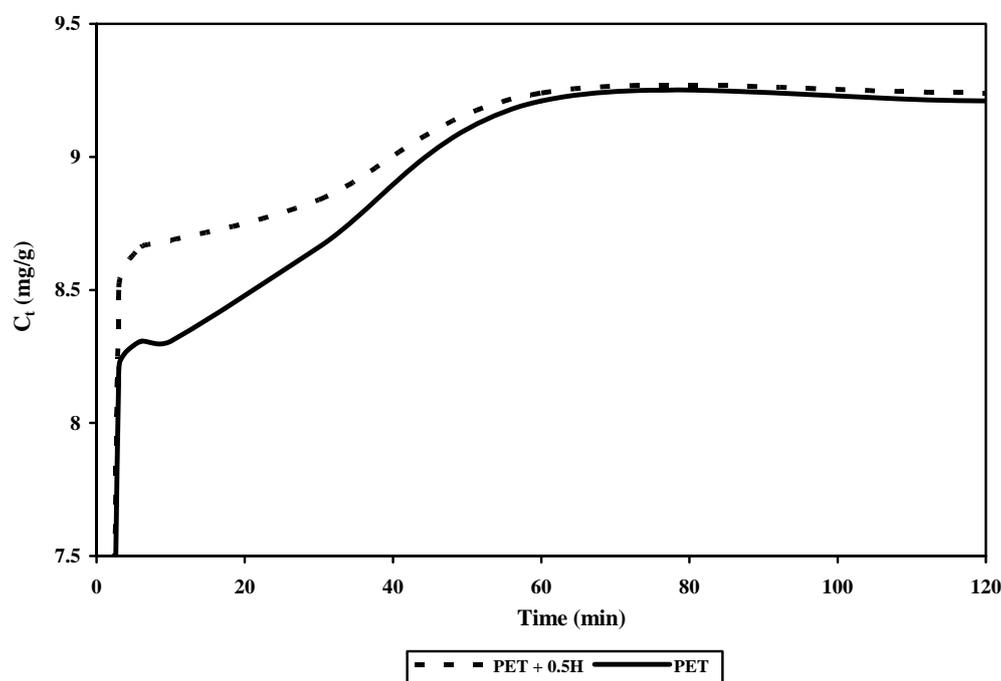


Figure 5: Rate of dyeing curves for unmodified and modified PET fibers with C.I. Disperse Red 324 at boiling temperature (initial amount of dye 10 mg/g fiber).

The D/r^2 was practically calculated to describe the diffusion of dyes into the fiber. By using Eq. (5) 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 slope of this equation [13]. The values of the diffusion coefficient (D/r^2) of the disperse dye on unmodified PET and modified PET fibers at boiling temperature are also reported in Table 1. According to Table 1, it was observed that the dyeing rate constant (k) for modified PET is more than unmodified PET and also modified PET had a higher diffusion coefficient value than unmodified PET at boiling temperature.

It is generally agreed that dyeing process involves three continuous steps. The first step is the diffusion of dye through the aqueous dyebath onto the fiber. The second step is the adsorption of dye into the outer layer of the fiber. And the last step is the diffusion of dye into the fiber inside from the adsorbed surface. The second step, the actual adsorption process, is generally assumed to be much more rapid than either of the other diffusion steps. Of the two diffusion steps, the diffusion into the

inner layer is much slower than the movement of dye through the aqueous solution due to the physical obstruction of dye diffusion caused by the network of fiber molecules. Therefore, dyestuff is first adsorbed on the surface of PET fiber and then dyestuff penetrates into the fiber. For the dye molecule to diffuse into the fiber, it is expected that the free volume could be formed within the substrate. This free volume is regarded as the void being temporarily formed within the fiber by the thermal movement of molecular chains and the dye molecules penetrate into this empty space. Therefore, the amount of dyestuff exhausted by fiber and the rate of dye adsorption depend on the structure of fiber, i.e. the free volume [14-16].

In this study, the amount of dyestuff exhausted by fiber as well as the rate of dye adsorption increase by incorporation of the Hybrane H1500 as an additive. This additive which reduces the glass transition temperature (T_g) of PET is indicative of increased mobility of the PET chains. This means that compounded PET become more flexible upon addition of the amorphous hyperbranched polymer additive [5]. Due to the fact that

the calculation method for diffusion coefficient of dye into fiber is strongly related to the amount of dye uptake by fiber, which is time-dependent, 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) .

The pronounced difference between the value of diffusion coefficient of dye into unmodified PET and compounded PET can be explained by the internal spaces of hyperbranched polymer. In fact, the internal spaces of hyperbranched polymer leading to increase the swelling property of compounded PET than that of unmodified PET. In other words, the internal structure of unmodified PET substrate during the dyeing process is more rigid than that of compounded PET that could lead to less penetration in comparison with compounded PET fiber. The SAXS study of the compounded PET has shown the shape of hyperbranched polymer. The finding obtained from SAXS is consistent with the results obtained through kinetics studies, i.e. the existence of internal spaces in the hyperbranched polymer.

It is no doubt that the crystallinity plays an important role in this issue and the higher degree of crystallinity of unmodified PET in comparison with compounded PET fiber reconfirms the findings.

Moreover, in the case of compounded PET, the accessibility of the fiber can be improved by incorporation of hyperbranched polymer that creates pathways in the polymer structure. Such pathways make the penetration of dye molecules toward the internal spaces of fibers more possible.

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4. Conclusion

This investigation involved the kinetic behavior of the dyeing of C.I. Disperse Red 324 on unmodified and compounded fiber grade PET at boiling temperature in absence of carriers. The kinetic parameters were discussed in terms of the relationship between the internal structure of fibers and the dye adsorption. We have found that the free volume in a polymer-dye system is the main factor determining the kinetic data. From the obtained results it is concluded that:

- The dyeing rate of modified PET was higher than that of unmodified PET and this was influenced by the hyperbranched polymer.
- The incorporation of 0.5% hyperbranched polymer markedly enhanced diffusion coefficient and dyeing rate constant of modified PET by C.I. Disperse Red 324.
- In respect of dyeing mechanism, while the dyeing sites are not available for both types of fibers, the hyperbranched polymer provides voids that could keep the dye molecules. SAXS studies also confirmed the voids in the hyperbranched polymer.
- The hyperbranched polymer improves the accessibility of the fiber sites, which is very important for effective dyeing procedure.

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