



Studying the Adsorption Behavior of a Disperse Dye on Polyethylene Terephthalate in Absence and Presence of a Nanostructured Hyperbranched Polymer

M. Ahani¹, M. Khatibzadeh^{2*} and M. Mohseni³

¹ M. Sc. Student, Amirkabir University of Technology, Department of Polymer Engineering and Color Technology, P.O.Box: 15875-4413, Tehran, Iran.

² Assistant Professor, Amirkabir University of Technology, Department of Polymer Engineering and Color Technology, P.O.Box: 15875-4413, Tehran, Iran.

³ Associate Professor, Amirkabir University of Technology, Department of Polymer Engineering and Color Technology, P.O.Box: 15875-4413, Tehran, Iran.

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ABSTRACT

Dyeing properties of modified polyethylene terephthalate with a polyesteramide hyperbranched polymer (HP) were investigated in terms of their thermodynamic parameters, including standard affinity ($-\Delta\mu^\circ$), enthalpy change (ΔH°) and entropy change (ΔS°). Results were then compared with corresponding properties of the virgin PET. The results showed that the isotherms were similar to that of virgin PET following as linear isotherm. The standard affinity of the dye to the modified samples showed higher value than that of virgin PET. The standard affinity of dye to the PET increased by the content of HP. The bath containing virgin PET displayed the highest negative values of the ΔH° and ΔS° , while that of the PET with 2% HP showed the lowest negative value. The surface structure and thermal behavior of the samples were determined by FTIR and DSC, respectively. DSC tests showed that the crystallinity and glass transition temperature of samples were decreased. Prog. Color Colorants Coat. 7(2014), 49-60. © Institute for Color Science and Technology.

1. Introduction

PET (Polyethylene terephthalate) is the most important synthetic polymer in the world due to its excellent physical and chemical properties, good chemical resistance, thermal stability and easy spinnability [1]. PET is an aliphatic-aromatic polymer and thermoplastic with maximum moisture regain of only 1% at 100%

relative humidity. It shows a hydrophobic nature due to its rigid structure. Figure 1 shows the chemical structure of PET [2].

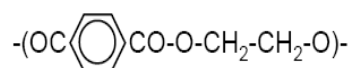


Figure 1: Chemical structure of PET.

*Corresponding author: khatib@aut.ac.ir

The two carbonyl functions together with the aromatic ring provide the structural rigidity of the macromolecule; little flexibility arises due to the presence of the ethylene group in the repeating unit. The polar ester groups in the PET give it strong crystallinity. PET consists of a two-phase structure: crystalline (35 % in vol.) and non-crystalline (65 % in vol.) [2]. The most important phase in determining the dyeability in a dyeing process is the amorphous region. In this case, the dye molecules are able to penetrate into the amorphous region and by cooling down the molecule can be trapped inside the PET [3]. It must be noted that below the glass transition temperature (T_g), the amorphous regions are glassy (and impermeable to the dye molecules) while above the T_g , this regions are rubbery. Disperse dyes are the most important dyes used for dyeing PET fibers. They have very low solubility (~5–30 mg/l), therefore can be considered almost insoluble in water in comparison to the so-called soluble dyes [4]. They either can sublime into PET fibers by heat through thermosol and/or thermofixation processes or be applied at high temperature/pressure or via carriers at boiling temperature by an exhaust process. The high crystallinity plus the hydrophobic nature and the compact molecular structure and lack of any reactive site in the molecule are the reasons that PET fibers cannot be dyed at boiling temperature in absence of suitable carriers. The carriers are necessary even though the temperature of the dyeing process is higher than T_g . It can be concluded that the dyeing temperature must always be higher than the T_g but due to the crystalline and compact nature of the polymer, some over-heating or the addition of specific plasticizing agents should be performed [5]. Many researchers have explored the problem of dyeing the PET fibers. The modification of PET in order to improve the PET fibers dyeability [6, 7] and a new method for dyeing of polyester fibers in which supercritical carbon dioxide (SCD) was used as a transfer medium [8] have been investigated. Besides, blending with other polymers such as hyperbranched polymer [9, 10] has been also reported. The modification of PET with the hyperbranched polymer provided a significant enhancement of dye uptake in PET fibers. However, improving the dyeability of PET was examined by measuring the surface reflectance function of colored samples, i.e. K/S value. Whereas, the employed function does not seem to be a suitable criterion for analytical evaluation of dyeing systems [11]. Few works have been done regarding the use of dendritic polymers for modifying the dyeing

behavior of other fibers. For example, a study was made by Burkinshaw *et al.* [12] to modify the dyeing behavior of reactive dyes on cotton. In another study, Burkinshaw *et al.* [13] showed that the incorporation of Hybrane PS2550 as a hyperbranched polymer into polypropylene prior to fiber spinning markedly enhanced the dyeability of PP by disperse dye.

Hyperbranched polymers belong to the class of synthetic tree-like macromolecules called dendritic polymers. They are polymers with densely branched structure and a large number of terminal groups. Dendritic polymers contain dendrimers which have completely-branched star-like topologies. Hyperbranched polymers have imperfectly branched or irregular structures [14]. Both dendrimer and hyperbranched polymer molecules are composed of repeating units emanating from a central core. The core is characterized by its functionality, which is the number of chemical bonds through which it can be connected to the external parts of the molecule. The functionality of the core is normally three (e.g. amine) or four (e.g. ethylenediamine). Through the bonds of the core, the layers of linear units (single monomers or linear chains) are attached to the core and each of these arms is terminated with a multifunctional branched unit. Larger molecules are created by adding shells of linear units to the end groups of the layer beneath. If all these units are perfectly attached to the molecule, a dendrimer is formed. In contrast, the absence of any of these units in the molecule will result in a hyperbranched polymer structure. A schematic representation of dendrimers and hyperbranched polymers is presented in Figure 2 [15, 16].

Dyeing technology is based on physico-chemical equilibrium processes, namely, diffusion and sorption of dye molecules. Therefore, determination of physicochemical parameters has a fundamental meaning for considering the dyeing mechanism [17].

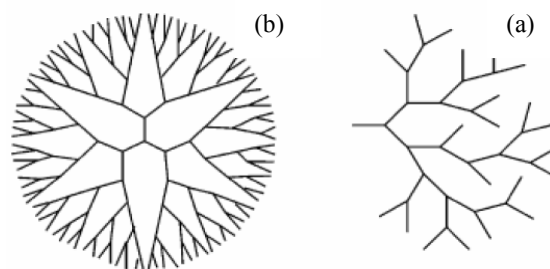


Figure 2: (a) Hyperbranched polymer; (b) Dendrimer.

In this study, the results of an investigation into the quantitative evaluation of the dyeing behavior and thermodynamic parameters of C.I. Disperse Blue 60 on the PET modified by a hyperbranched polymer has been reported. The results have then been compared with corresponding parameters obtained for the non-modified PET. Meanwhile, the evolution of the surface structure of the samples was analyzed using Fourier Transform Infrared Spectroscopy (FTIR). Thermal analysis by Differential Scanning Calorimetry (DSC) was used to probe the effects of hyperbranched polymer on crystallinity and glass transition temperature (T_g) of modified PET fibers.

2. Experimental

2.1. Materials

PET chips (Zimmer Specification, Germany) were provided by Shahid Tondgoyan Petrochemical Company (Iran) as shown in Table 1.

Hybrane H1500, a nanostructured hyperbranched polymer was provided by DSM, Netherlands, the specification and chemical structure this polymer shown in Table 2 and Figure 3, respectively.

Table 1: PET fiber grade chips.

Description	Expected
Intrinsic viscosity (dl/g)	0.60-0.66
Water content (%wt)	0.25

Table 2: Hybrane H1500 specification.

Chemical name	Hyperbranched polyesteramide
Physical appearance	Solid, as powder or lumps
Color	Off-white
Odor	None
Molecular weight	~1500
Molecular formula	$(C_6H_{15}NO_2 \cdot C_8H_{10}O_3)_x$
Boiling point (range)	>250°C
Solubility (20°C)	Insoluble in water, soluble in ethanol (>500 g/l)
Glass transition temperature (T_g)	78°C

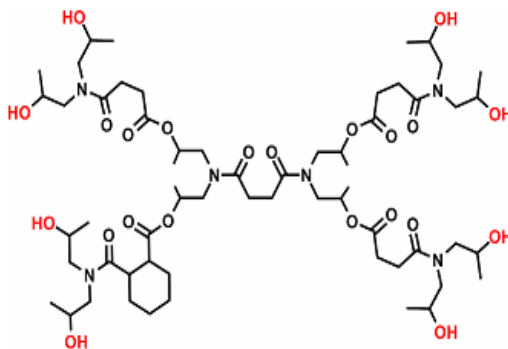


Figure 3: Chemical structure of Hybrane H1500.

The selected disperse dye for this work was the commercial grade of C.I. Disperse Blue 60 named Terasil Blue BGE without further purification that was purchased from Ciba Company, Iran. The chemical structure of this dye is given in Figure 4. The maximum absorption wavelength of the dye measured by UV-Vis spectrophotometer (Color-Eye 7000A) was obtained at 670 nm.

2.2. Preparation of samples

PET chips were dried in an oven at 80°C for 24 hours prior to mixing. An internal mixer (Brabender Plasticorder W50, Brabender Company, Germany) was used to prepare three melted samples including virgin PET, PET plus 0.5 and 2% hyperbranched polymer, respectively. The mixing temperature was set at 255°C at the speed of 60 rpm for 5 minutes. Then, laboratory mixing extruder (LME) was used to provide fibers from mentioned melted samples (at temperature of 255°C and speed of 60 rpm). Before the dyeing process, the fibers were washed in water with a nonionic detergent (Lanasan LT) in order to eliminate the excess amount of substances on the fiber. Washing was carried out with 2 ml/l of detergent and a 50:1 liquor-to-goods ratio at 60°C for 30 minutes. After washing, the samples were rinsed several times with lukewarm water and dried at room temperature.

2.3. Characterization of prepared samples

2.3.1. Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra were recorded at 4 cm⁻¹ resolution on Bomem Hartman & Braun FTIR Spectrophotometer in the range of 500-4000 cm⁻¹. The samples were analyzed from KBr pellets.

2.3.2. Differential Scanning Calorimetry (DSC)

DSC measurements of samples were carried out on a Mettler Toledo Differential Scanning Calorimetry. These measurements were performed in nitrogen atmosphere at heating and cooling rates of 10°C/min. The samples were heated from 0 to 300 °C, holding for 5 minutes to eliminate thermal history effects and cooled down to 0 °C, then heated up to 300 °C again for the second scan.

All the data were collected by the second scan. The glass transition temperature (T_g), the crystallization temperature (T_c), the melting temperature (T_m) and the apparent enthalpy of fusion (ΔH_f) of samples were calculated from the DSC thermographs. The percent of crystallinity of the samples were calculated by Eq. (1), using the ratio of their enthalpy of fusion (ΔH_f) to the enthalpy of fusion of the PET crystal with a value of $\Delta H=140$ J/g [18].

$$\text{Crystallinity} = \Delta H_f / \Delta H \quad (1)$$

2.3.3. Dynamic Mechanical Thermal Analysis (DMTA)

Dynamic mechanical thermal analysis (DMTA) was carried out with a DMTA Tritec 2000-TRITON in the tensile mode. Dynamic loss ($\tan \delta$) was determined at a frequency of 1 Hz and a heating rate of 10 °C/min as a function of temperature in the range of 0 to 300°C.

2.4. Dyeing method and adsorption isotherm

Three prepared mentioned fibers (0.1 g) were individually dyed using a laboratory dyeing machine (IR Elite Lab. Dyeing Machine, KMS COLORTECH SERVICE Co., Hong Kong (China)), 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 130°C with the liquor-to-goods ratio of 1000:1, until equilibrium adsorption was obtained.

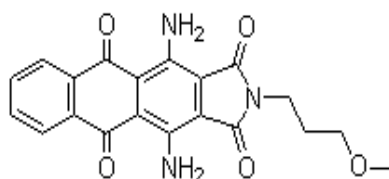


Figure 4: C.I. Disperse Blue 60.

The state of equilibrium was achieved after 4-5 hours, depending on temperature. Dyeing was started at ambient temperature and increased to 80, 100 and 130°C at a constant rate of 2°C/min and held at these temperatures for 300 minutes. Finally, the amount of dye between the bath ($[C]_s$) and the fiber ($[C]_f$) in equilibrium were determined at mentioned dyeing temperatures. The measurements were carried out with a UV-Vis spectrophotometer (Color-Eye 7000A), at the wavelength of maximum absorption of this dye, $\lambda_{max} = 670$ nm. By recording the amount of absorbed dye on fibers versus the amount of remained dye in the corresponding dyebaths, the adsorption isotherms were obtained.

2.5. Partition coefficient and standard affinity

The partition coefficient (K) of the dye between the fiber substrate ($[C]_f$) and the adsorption solution ($[C]_s$) was obtained from the adsorption isotherms. The standard affinity ($-\Delta\mu^\circ$) of the dye was calculated using Eq. (2) as below:

$$-\Delta\mu^\circ = RT \ln ([C]_f / [C]_s) = RT \ln K \quad (2)$$

where $-\Delta\mu^\circ$ is standard affinity (cal mol^{-1}); R shows the gas constant ($1.9872 \text{ cal mol}^{-1} \text{ K}^{-1}$); T represents the absolute temperature (K); $[C]_f$ and $[C]_s$ indicate the dye concentration in fiber (mol kg^{-1}) and in adsorption solution (mol L^{-1}), respectively, and K shows the partition coefficient.

2.6. Enthalpy change

The enthalpy change (ΔH°) in adsorption process was obtained from the empirical plot that shows the relationship between $\Delta\mu^\circ/T$ and $1/T$ using Eq. (3):

$$\Delta H^\circ/T = \Delta\mu^\circ/T + C \quad (3)$$

where ΔH° is heat of adsorption (cal mol^{-1}) and C

represents the integral constant.

2.7. Entropy change

The entropy change (ΔS°) was calculated using Eq. (4):

$$\Delta\mu^\circ = \Delta H^\circ - T\Delta S^\circ \quad (4)$$

where ΔS° indicates the change in entropy ($\text{cal mol}^{-1} \text{ K}^{-1}$).

3. Results and discussion

3.1. FTIR results

In the first step it was necessary to record the FTIR spectra of the virgin PET (Figure 5(a)) and the pure hyperbranched polymer (Figure 5(b)) in order to be used for comparison with the FTIR spectra of the modified samples. The FTIR spectra of the modified PET fibers are shown in Figures 6(c-d). The FTIR results showed that the presence of hyperbranched polymer was detected in all the modified samples. In almost all the cases (PET + 0.5% HP and PET + 2% HP) the presence of the hyperbranched polymer was proved by the presence of the peaks at 1400-1500 and 1600-1700 cm^{-1} . These peaks belong to the pure hyperbranched polymer of the modified PET and it just shows the superimposition of the spectra of the pure PET and pure hyperbranched polymer. So no interaction has occurred.

3.2. Crystallinity and glass transition temperature: DSC results

Thermal properties of the modified PET samples may be changed by corporation the hyperbranched polymer as an additive to the virgin PET. The glass transition temperature (T_g), the melting point (T_m) and the apparent enthalpy of fusion (ΔH_f) were determined from the DSC thermographs. Figure 6 presents DSC curves for the pure and modified PET fibers during heating at a rate of 10 $^\circ\text{C}/\text{min}$. Table 3 reports various data obtained from DSC analyses of virgin and modified PET fibers.

Table 3: Thermal behavior of two loads of Hyperbranched polymer in modified PET fiber using DSC technique.

Sample	Crystallinity	T_m ($^\circ\text{C}$)	T_g ($^\circ\text{C}$)
PET	44%	257.21	80.07
PET + 0.5% HP	41.65%	255.05	76.70
PET + 2% HP	38%	253.47	72.49

It was found that the glass transition temperature of virgin PET fiber was changed from 80.07°C to 76.7°C and 72.49°C by adding 0.5% and 2% hyperbranched polymer to the virgin PET, respectively. It is concluded

that the glass transition temperature decreases as the content of hyperbranched polymer increases. This means that the samples become more flexible upon addition of the amorphous hyperbranched polymer.

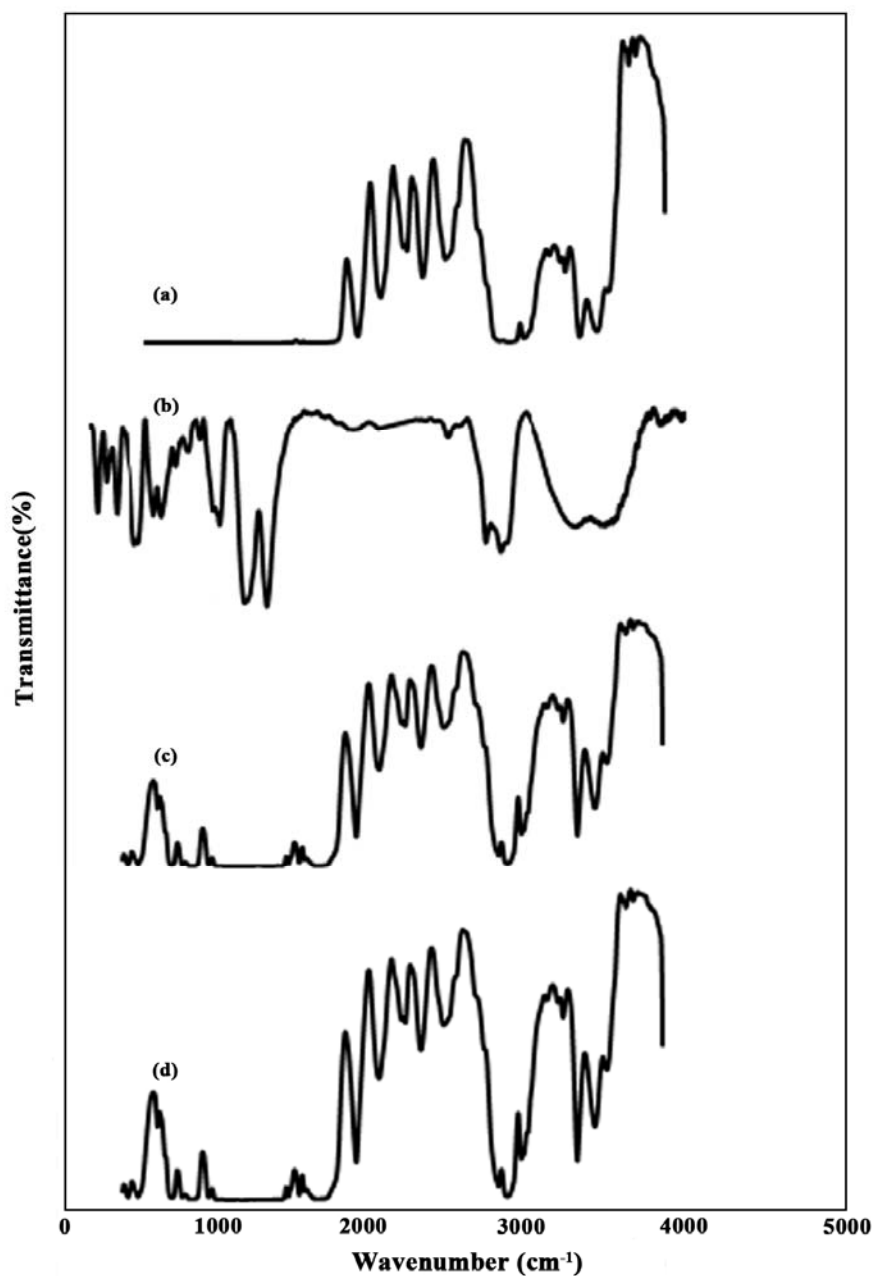


Figure 5: FTIR spectra of (a) virgin PET, (b) pure HP, (c) PET + 0.5% HP and (d) PET + 2% HP.

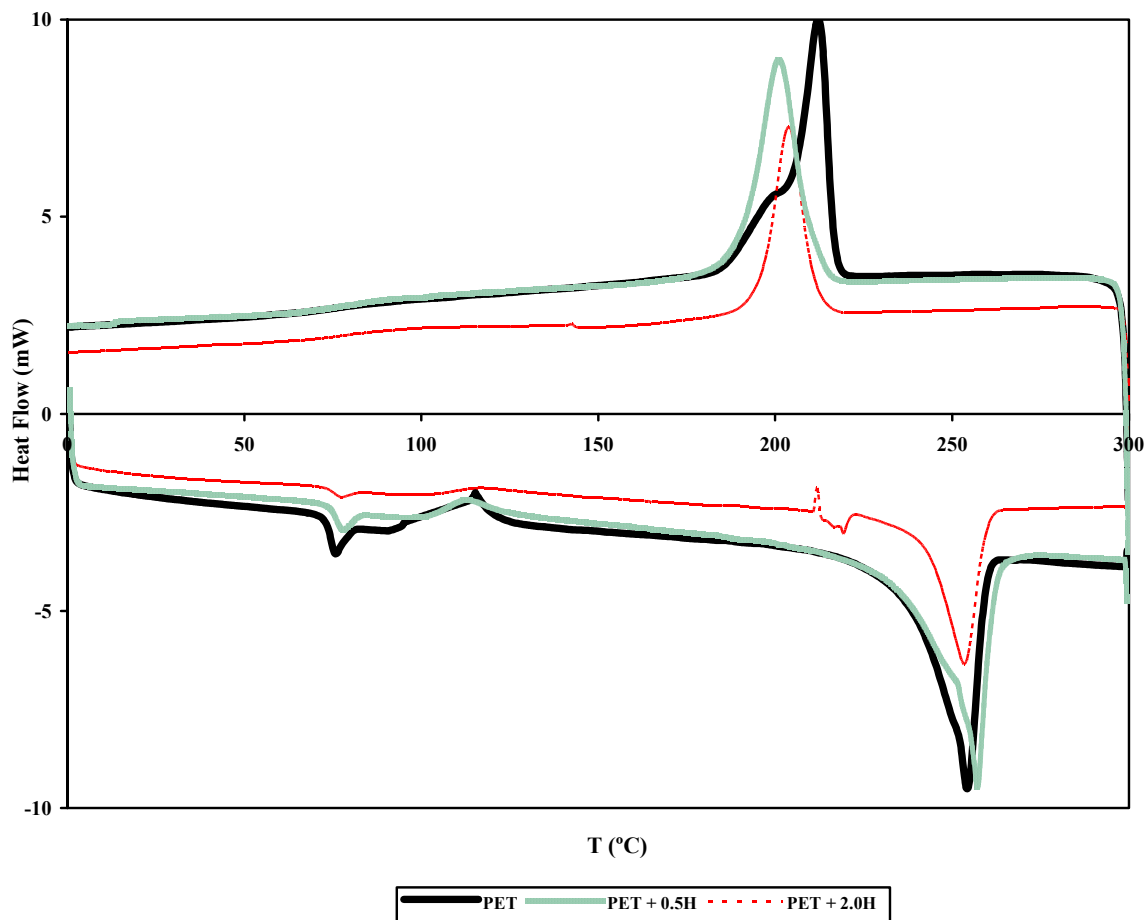


Figure 6: DSC curves of pure and modified PET fibers.

For further investigations, the crystallinity of each sample was calculated from the heat of fusion during heating as shown in Table 3 and it decreased with the addition of hyperbranched polymer content in the virgin PET. As shown in Table 3, the crystallinity was 44% in virgin PET fiber. When 0.5% and 2% hyperbranched polymer were added to the virgin sample, the crystallinity content of modified PET fell to 41.65 and 38%, respectively. As crystallinity was decreased, the amorphous parts were increased, and the dye uptake could increase accordingly.

3.3. DMTA results

The DMTA results of all samples are presented in Figure 7 in terms of temperature dependence of the loss factor, $\tan \delta$. Figure 7 shows that the modified samples have only one relaxation peak, the primary relaxation peak

associated with glass transition temperature. This represents that modified samples have only one maximum $\tan \delta$, indicating that a homogenous compounding has occurred. In other words, the hyperbranched polymer has been dispersed properly in PET and is able to introduce a homogenous compound with a single glass transition temperature.

These results indicate that the blends are partially miscible. Interestingly, with increasing the hyperbranched polymer content, the glass transition temperature of modified PET fibers tends to shift towards lower temperatures. Thus, the decreased value of T_g resulting from the addition of the hyperbranched polymer confirms that the mobility of polymeric chains has greatly increased the softness and flexibility of the samples.

3.4. Adsorption isotherm and standard affinity

Adsorption isotherms known as equilibrium data are the fundamental requirements for the design of adsorption systems. The standard affinity ($-\Delta\mu^\circ$) of the dye towards fiber substrate is the most basic and important thermodynamic parameter. This parameter can be defined as a difference between the chemical potential of the dye in the fiber and that of the dye in the solution in a standard state. This quantity is the measure of the

tendency of dye to move from its standard state of the adsorption solution to its standard state of the fiber substrate [19, 20]. Hence, in order to calculate the standard affinity of C.I. Disperse Blue 60 towards virgin and modified PET fibers, the isotherm data of dye adsorption were obtained at several different temperatures.

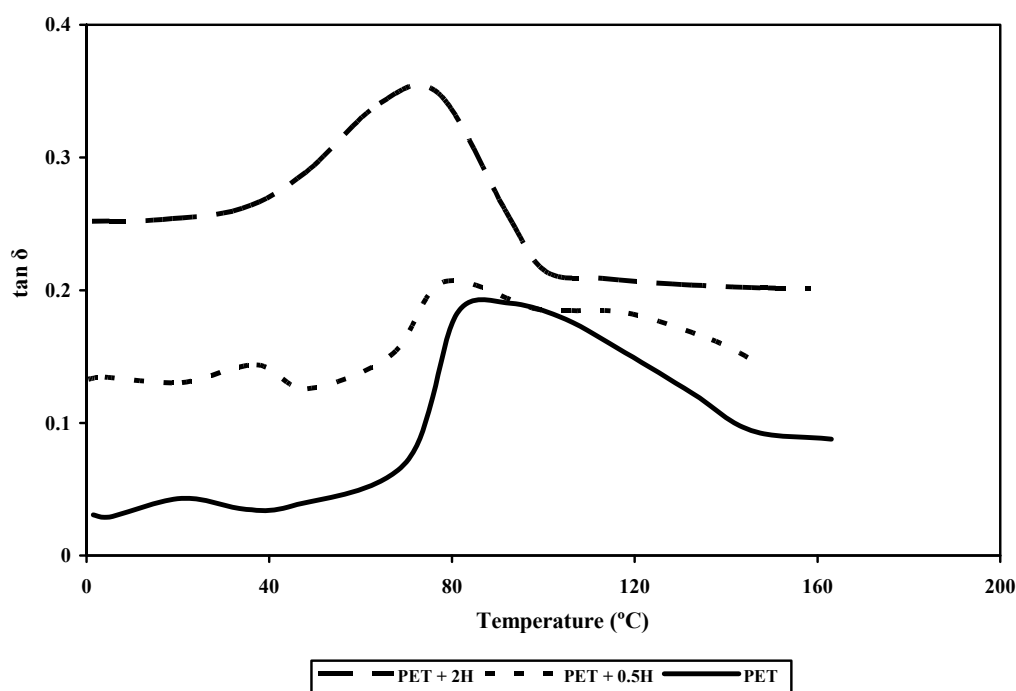


Figure 7: Temperature dependence of the loss factor ($\tan \delta$) for the virgin and modified PET fibers.

Table 4: The partition coefficient (K) and the standard affinity ($-\Delta\mu^\circ$) of C.I. Disperse Blue 60 on virgin and modified PET at different temperatures.

Temp (°C)	PET		PET+0.5%H		PET+2.0%H	
	K	$-\Delta\mu^\circ$ (cal mol ⁻¹)	K	$-\Delta\mu^\circ$ (cal mol ⁻¹)	K	$-\Delta\mu^\circ$ (cal mol ⁻¹)
80	35.22	2498	39.50	2578	45.42	2676
100	22.44	2306	25.07	2388	27.43	2455
130	10.32	1869	13.45	2081	17.67	2300

Figure 8(a-c) shows the adsorption isotherms of C.I. Disperse Blue 60 for virgin and modified PET fibers at 80, 100 and 130°C. This figure represents the linear relationship between the dye concentration in dyebath and the adsorption amount of the dye on fibers. This relationship obeys the Nernst's adsorption model which commonly represents the dyeing mechanism between disperse dye and PET fibers [17]. The slopes of the straight lines in the isotherms are the partition coefficients (K) of the dye between the dyeing solution and the fibers. The standard affinity is determined approximately using partition coefficient.

From Eq. (2), the standard affinity can be calculated as summarized in Table 4. It is found from Table 4 that the standard affinities of PET plus 0.5 and 2% hyperbranched polymer are higher than those of virgin PET. This finding explains that the dye has higher tendency to move from the dyeing solution to modified PET fibers compared to virgin PET. The tendency of the dye to move from the adsorption solution to PET increased with increasing the hyperbranched polymeric additive percentage. The negative value of the standard affinity ($\Delta\mu^\circ$) indicated the spontaneous nature of dye adsorption on the fibers. As the temperature increases, the standard affinity decreases in all fibers. This observation can be attributed to the adsorption of dyes towards fiber which is an exothermic process. Higher dyeing temperature gives a negative effect on the thermodynamic adsorption [19].

3.4. Enthalpy and entropy change

The enthalpy change (ΔH°) is considered as the measure of the adsorption strength of dyes on the substrate. Meanwhile, the entropy change (ΔS°) in adsorption process reveals the entropy difference of the

dye molecules between the fibers and the adsorption medium. In most adsorption processes, the entropy change shows negative values, because adsorbed dye molecules become more restrained within the fiber molecules than adsorption medium. Therefore, the value of the entropy change could be considered as the measure of immobility of dyes within the fiber molecules [19, 20]. As expected from Eq. (3), the relationship between $\Delta\mu^\circ/T$ and $1/T$ must show linear relationship. From the slopes of the straight lines, the enthalpy change can be calculated. Meanwhile, Eq. (4) showing the linear relationship between $\Delta\mu^\circ$ and T , the entropy change can also be obtained.

The enthalpy and the entropy change which obtained from this study are presented in Table 5. According to Table 5, virgin PET fiber showed higher negative values of ΔH° ($-7013 \text{ cal mol}^{-1}$) and ΔS° ($-12.74 \text{ cal mol}^{-1} \text{ K}^{-1}$), while PET plus 2% hyperbranched polymer showed lower negative values.

The enthalpy change shows the amount of the released thermal energy when dye molecules are adsorbed into polymer chains. The larger negative value represents that the dye molecules are more strongly embedded within the polymer molecules. Hence, it could be concluded from Table 5 that modified PET fibers include more flexible units due to the presence of a noncrystallisable component in the formulation. Accordingly, modified PET fibers showed much more dyeability than that of virgin PET. On the other hand, it can be attributed mainly to a reduction in T_g in comparison with virgin PET, and this characteristic gives higher flexibility to chains of modified PET than that of virgin PET. In Table 5, the entropy change of virgin PET fiber showed the largest negative value among other fibers.

Table 5: The enthalpy change (ΔH°) and the entropy change (ΔS°) of C.I. Disperse Blue 60 on virgin and modified PET fibers.

Parameters	PET	PET+0.5%H	PET+2%H
ΔH° (cal mol ⁻¹)	-7013	-6119	-5319
ΔS° (cal mol ⁻¹ K ⁻¹)	-12.74	-9.96	-7.33

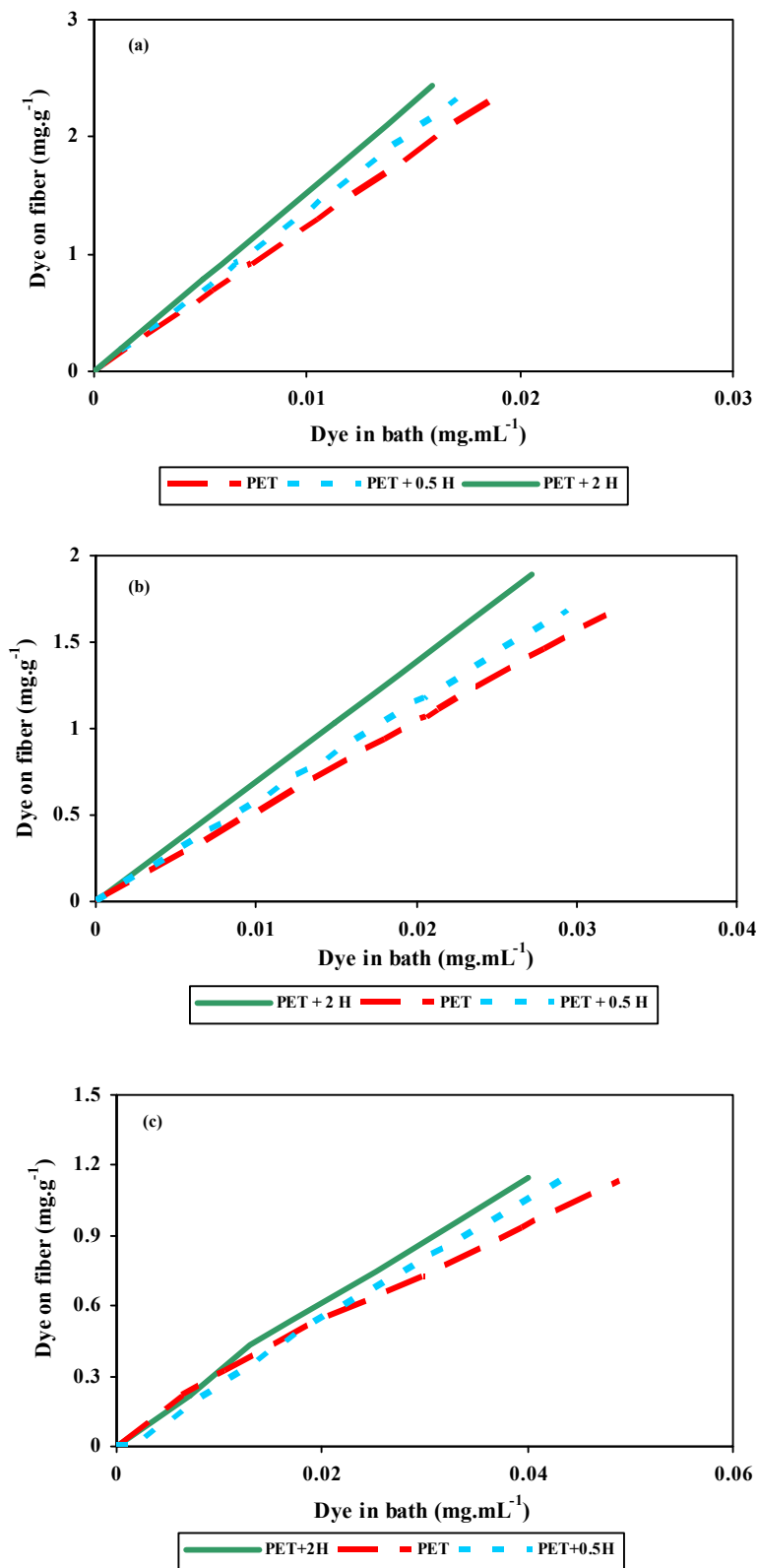


Figure 8: Adsorption isotherms of C.I. Disperse Blue 60 on virgin and modified PET at 80 °C (a), 100 °C (b) and 130 °C (c).

The larger negative value of the entropy change represents the phenomenon that the mobility of the dye molecules significantly decreased after dyeing. This observation suggests that the dye molecules inside virgin PET fiber have the most immobilized state.

4. Conclusions

In this study, the thermodynamic parameters of disperse dye adsorption on modified PET fiber with a nanostructured hyperbranched polymer were investigated. The determination of some important thermodynamic parameters revealed the practical significance of the dye on the fibers. The FTIR analysis showed the presence of some peaks which existed in the modified PET samples spectrum. Thermal analysis by Differential Scanning Calorimetry (DSC) was used to probe the effect of hyperbranched polymer on crystallinity and glass transition temperature of modified samples. The presence of the hyperbranched polymer decreased the glass transition temperature and

the crystallinity of the modified samples relative to the virgin PET. The standard affinities of disperse dye on modified PET were higher than those of virgin PET. In the case of enthalpy change and entropy change, virgin PET fiber showed higher negative values of ΔH° and ΔS° , while PET fiber with 2% hyperbranched polymer showed the lowest negative values. The various values of thermodynamic parameters have shown that the application of the disperse dye on all fibers is exothermic. Modification of PET fiber with hyperbranched polymer is thus a way to increase the affinity between the disperse dye and the PET fiber. The results from this study should help to underpin future improved practical applications of dyeing of PET fibers.

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