

Blends of Polyethylene Terephthalate (PET) and Nanostructured Hyperbranched Polyesteramide for Improvement the Dyeability of PET: Thermodynamics

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Incorporating Hybrane H1500 as a nanostructured hyperbranched polyesteramide into polyethylene terephthalate (PET) enhances the dyeability of PET with C.I. Disperse Blue 56. The results show that the disperse dye display much greater substantivity toward the modified PET sheets compared to virgin PET one. DSC tests show that the crystallinity of modified PET sheets has slightly decreased. The main purpose of this work was to determine the dyeing mechanism of disperse dye on the modified PET using hyperbranched polyesteramide by study the adsorption properties in the infinite dye bath at different temperatures. In fact, a few of the thermodynamic parameters of dyeing such as the equilibrium adsorption isotherm, standard affinity, enthalpy and entropy changes were studied. The bath containing virgin PET displays the highest negative values of the enthalpy change and entropy change, while the bath containing the modified PET with 2 wt% hyperbranched polyesteramide shows the lowest negative values of them.

Keywords: Polyethylene terephthalate (PET) sheet, Nanostructure, Hyperbranched polyesteramide, Thermodynamic parameters, Dyeing, Disperse dye.

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1. INTRODUCTION

In textile industry, PET (Polyethylene terephthalate) has widely been used as a raw material for woven fabrics and nonwoven because of its excellent physical and chemical properties. PET is the most popular synthetic polymer because of its excellent chemical resistance, thermal stability and easy spinnability [1]. Disperse dyes are the most important dyes which have been used for dyeing PET. The biggest complaint about PET is that it absorbs very little dye at boiling temperature without using carriers. Therefore, using carriers or high temperature/pressure is necessary for dyeing PET with disperse dyes. The high crystallinity, hydrophobic nature and compact molecular structure as well as does not contain any reactive site in the molecule are the reasons that PET cannot be dyed in absence of carriers [2]. In order to improve such disadvantage, a variety of methods have been proposed [3-5]. In one study, khatibzadeh *et al.* used a hyperbranched polymer to improve the dyeability of fiber grade PET [6].

Hyperbranched polymers have a large number of functional groups, low melt viscosities and a globular three dimensional structure. Due to these structural characteristics, their properties largely deviate from linear polymers. They have cavities in their molecule which enable them to trap guest molecules by specific interactions. Due to their globular structure, dendrimers and hyperbranched polymers are discussed as carrier molecules. Furthermore, the low melt viscosity of hyperbranched polymers offers applications as melt modifiers or blend components [7-9].

Because dyeing is a process, the state of equilibrium is reached after a time period. Therefore, determination of thermodynamic parameters has a fundamental meaning for considering the dyeing mechanism. In this study, the results of an investigation into the quantitative evaluation of the dyeing behavior and thermodynamic parameters of C.I. Disperse Blue 56 on modified PET sheets with hyperbranched polymer were studied. The results have been then compared with corresponding parameters obtained for the unmodified PET.

2. EXPERIMENTAL

2.1 Materials

Chips of PET (Zimmer Specification, Germany) were supplied by Shahid Tondgoyan Petrochemical Company (Iran) and were a fiber grade material with an intrinsic viscosity of 0.60 dl g⁻¹, water content 0.25 %wt and melting point 250°C.

Hybrane H1500, a nanostructured hyperbranched polyesteramide was provided by DSM, Netherlands. Its molecular formula is (C₆H₁₅NO₂.C₈H₁₀O₃)_x and its molecular weight is 1500 g mol⁻¹.

Throughout the experiments, the selected disperse dye (C.I. Disperse Blue 56 named as Serilene Blue RL) without further purification was purchased from Yorkshire Group, UK. The employed disperse dye belongs to low energy group of disperse dyes. This dye is an anthraquinone dye and its molecular weight is 304.69 g mol⁻¹.

2.2 Melt processing

Chips of PET were dried in an oven at 80°C for 24 hours prior to blending. An internal mixer (Brabender Plasticorder W50, Brabender Company, Germany) was used for mixing samples including various loads ranging from 0.5 to 3.0 wt% of Hybrane H1500 with PET. The mixing temperature was set at 250°C at the speed of 60 rpm for 5 minutes. Sheets of 1 mm thickness were prepared by hot pressing the resultant compounded mixtures. Each sample was pressed for 5 minutes at a pressure of 140 bar and a temperature of 250°C. The press was subsequently cooled to 100°C using cold water. Then, sheets were scoured in a solution containing 2 g/l of nonionic surfactant at 60°C for 30 minutes. The liquor-to-goods ratio was 500:1. Sheets were then washed completely in cold water and dried in the open air.

2.3 Characterization of prepared samples

2.3.1 Atomic Force Microscopy (AFM)

Tapping mode AFM (Ambios Tech (USA)) was used to characterize the samples. A scanning probe microscope was operated in tapping mode under ambient conditions with commercial silicon microcantilever probes. Phase images were obtained using a resonance frequency of approximately 300 KHz.

2.3.2 Attenuated Total Reflectance (ATR-FTIR)

ATR-FTIR measurements on samples were carried out on a Bomem Hartman & Braun FTIR Spectrophotometer. The samples were analyzed in the reflectance mode in the range of 400-4000 cm^{-1} .

2.3.3 Differential Scanning Calorimetry (DSC)

Crystallinity and the glass transition temperature (T_g) of the samples was calculated by Mettler Toledo Differential Scanning Calorimetry (DSC) instrument under nitrogen. The sample pan and the reference pan were heated from 0 to 300°C at the rate of 10 °C/min.

2.4 Adsorption amount of the dye on to sheet

For determination of the thermodynamic parameters dyeing, the dye concentration in the dyebath was measured using spectrophotometer (Color-Eye 7000A). The decrease in the total amount of dye in the dyebath was considered as the amount of dye on the sheet.

2.5 Dyeing thermodynamic parameters

Using a laboratory dyeing machine (IR Elite Lab. Dyeing Machine, KMS Colortech Service Co., Hong Kong), 0.1 g of each sheets 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 temperatures 80, 100 and 130°C with the liquor-to-goods ratio 1000:1, until equilibrium adsorption was obtained. Dyeing started at ambient temperature increasing to 80, 100 and 130°C at a constant rate of 2 °C/min and held at these temperatures for 300 minutes.

2.5.1 Dye adsorption isotherms

Using recording the amount of adsorbed dye on sheets ($[C]_s$) versus the amount of remained dye in the corresponding dyebaths ($[C]_b$), the adsorption isotherms were obtained.

2.5.2 Partition coefficient and standard affinity

The partition coefficient (K) of the dye between the sheet ($[C]_s$) and the adsorption solution ($[C]_b$) was obtained from the adsorption isotherms. The standard affinity ($-\Delta\mu^\circ$) of the dye to sheets was determined by Eq. (1).

$$-\Delta\mu^\circ = RT \ln ([C]_s/[C]_b) = RT \ln K, \quad (1)$$

where $-\Delta\mu^\circ$ is the standard affinity (cal mol^{-1}); R is the gas constant ($1.9872 \text{ cal mol}^{-1} \text{ K}^{-1}$); T represents the absolute temperature (K); $[C]_s$ and $[C]_b$ indicate the dye concentrations in sheets (mol/kg sheet) and in baths (mol l^{-1}) after achieving dyeing equilibrium, respectively and K is the partition coefficient.

2.5.3 Enthalpy change

According to Eq. (2), the enthalpy change (ΔH°) could be simply determined by plot of $\Delta\mu^\circ/T$ versus $1/T$.

$$-\Delta H/T = \Delta\mu/T + C, \quad (2)$$

where ΔH° is heat of adsorption (cal mol^{-1}) and C represents the integral constant.

2.5.4 Entropy change

The entropy change (ΔS°) was calculated using Eq. (3).

$$\Delta\mu^\circ = \Delta H^\circ - T\Delta S, \quad (3)$$

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

3. RESULTS AND DISCUSSION

3.1 AFM results

The evolution of the morphology of the sheet surfaces as observed by AFM is illustrated in Figure 1a-d which is the original scans without any filtering. The phase contrast image for virgin PET shows a relatively smooth and uniform surface without any nanoparticle. For modified PET sheets using 1 and 2 wt% hyperbranched polymer, a few number of light-colored particles were observed which is indicative of the existence of hyperbranched polymer. These observations confirm that no aggregates were formed and there is a complete uniform surface. Some aggregations were observed in sample containing 3 wt% hyperbranched polymer. Therefore, dyeing on modified PET sheets with 0.5, 1 and 2 wt% hyperbranched polymer was performed.

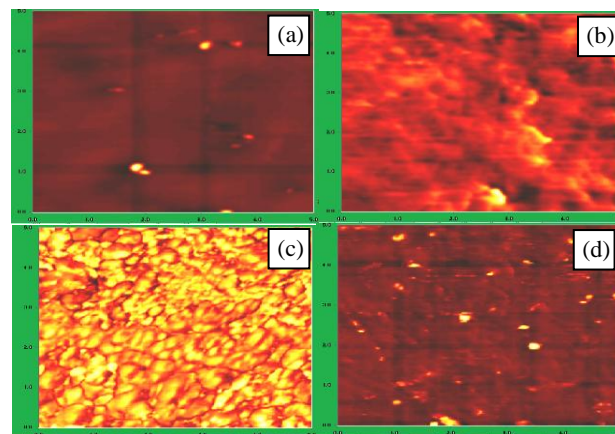


Fig. 1 – AFM images virgin PET (a), PET + 1H (b), PET + 2H (c) and PET + 3H (d)

3.2 ATR-FTIR results

In the first step it was necessary to record the ATR-FTIR spectra of the virgin PET sheet (Figure 2a) and the pure hyperbranched polymer (Figure 2b) in order to be used for comparison with the ATR-FTIR spectra of the modified sheets. The ATR-FTIR spectra of the modified PET sheets are shown in Figure 2c-e. The ATR-FTIR results showed that the presence of hyperbranched polymer was detected in all the modified samples. In almost all the cases 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 sheets and it just shows the superimposition of the spectra of the virgin PET and pure hyperbranched polymer. So no interaction has occurred.

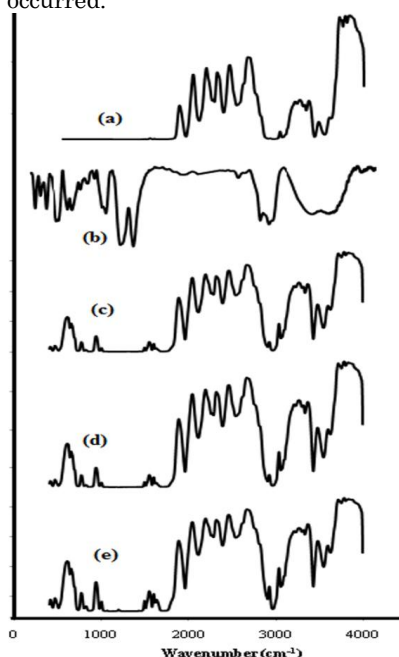


Fig. 2 – ATR-FTIR spectra of virgin PET (a), pure hyperbranched polymer (b), PET + 0.5H (c), PET + 1H (d) and PET + 2H (e)

3.3 DSC results

By adding the hyperbranched polymer to the virgin PET, the thermal properties of the modified PET samples may be changed. It can be found from Figure 3 that as the content of hyperbranched polymer increases, the glass transition temperature decreases. This means that samples become more flexible upon addition of the amorphous hyperbranched polymer. For further investigations, the crystallinity for each sample was calculated as shown in Figure 3 and it decreased with the addition of hyperbranched polymer content in the virgin PET. As crystallinity is decreased, the amorphous parts are increased, and the dye uptake is increased accordingly.

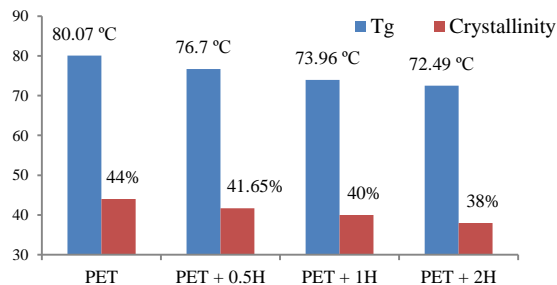


Fig. 3 – Glass transition temperature (T_g) and crystallinity (%) of virgin and modified PET sheets.

3.4 Thermodynamic parameters

3.4.1 Adsorption isotherm and standard affinity

The standard affinity ($-\Delta\mu^0$) of the dye in dyeing solution towards substrate is the most important thermodynamic parameter of dyeing. This parameter is defined as a difference between the standard chemical potential of the dye in the sheet phase (μ_s) and the standard chemical potential of the dye in the solution phase (μ_b) at the equilibrium state [10-12]. This parameter is the measure of the tendency of the dye to move from its standard state of the dyeing solution to its standard state of the sheet [10-12]. In order to calculate the standard affinity of C.I. Disperse Blue 56 towards virgin PET sheet as well as modified PET ones, the adsorption isotherm data of dye were obtained at three various temperatures 80, 100 and 130°C. Figure 4a-c shows the adsorption isotherms for virgin and modified PET sheets at various temperatures. Results in Figure 4a-c suggest a linear trend (Nernst isotherm) for both PET and sheets containing hyperbranched polymer. According to the type of the isotherm, it can be said that in respect of dyeing mechanism, while the dyeing sites are not available for samples, the hyperbranched polymer provides voids in the modified PET sheets that could trap the dye molecules. This phenomenon increases along with increasing hyperbranched polymer.

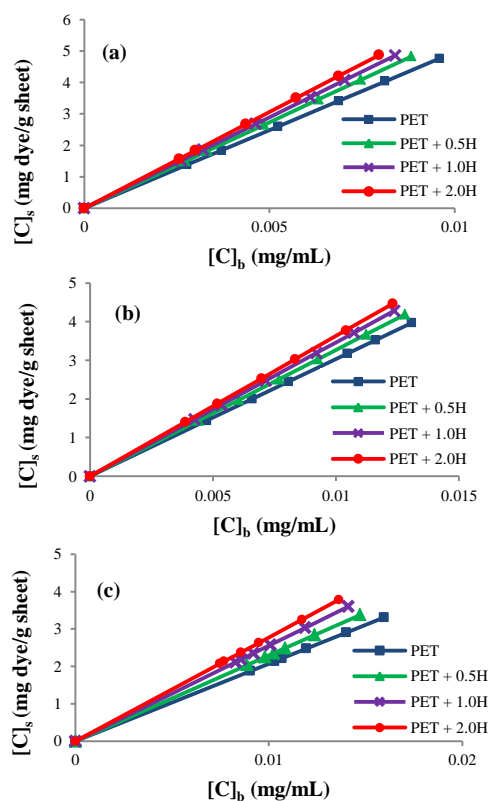


Fig. 4 – Adsorption isotherms of C.I. Disperse Blue 56 on virgin and modified PET sheets at 80(a), 100(b) and 130°C(c)

The partition coefficient (K) of the dye between the dyeing solution and the substrate is obtained from the slope of the adsorption isotherm. It can be seen in Table 1 that K values for modified PET sheets are higher than that of the virgin PET one. Using K as Nernst constant, the standard affinity could be calculated ac-

ording to Eq. (1). The values of standard affinity are shown in Table 1. As shown in Table 1, the standard affinities of dye to modified PET sheets are higher than that to virgin PET one. As the content of nanostructured hyperbranched polymer of samples increased, the standard affinity of the modified PET sheets increased. This finding explains that the dye has higher tendency to move from the dyeing solution to the modified PET substrates in comparison with virgin PET one. The partition coefficients of C.I. Disperse Blue 56 on all of the samples decreased when the temperature increased. The adsorption of dyes on substrate is an exothermic reaction process [10-12], therefore raising the temperature of dyeing leads to lower affinity.

Table 1 – Partition coefficient (*K*) and standard affinity ($-\Delta\mu^0$) of C.I. Disperse blue 56 on virgin and modified PET sheets.

Temperature	80°C		100°C		130°C	
	<i>K</i>	$(-\Delta\mu^0)$ (cal mol ⁻¹)	<i>K</i>	$(-\Delta\mu^0)$ (cal mol ⁻¹)	<i>K</i>	$(-\Delta\mu^0)$ (cal mol ⁻¹)
PET	49.67	2739.56	30.36	2529.89	20.73	2427.81
PET + 0.5H	54.69	2807.10	32.69	2584.70	22.94	2508.94
PET + 1.0H	57.87	2846.75	34.62	2627.22	25.51	2593.98
PET + 2.0H	61.23	2886.34	36.30	2662.34	27.74	2661.09

3.4.2 Enthalpy and entropy change

The enthalpy change (ΔH^0) is regarded as the measure of the adsorption strength of dyes [10-12]. The entropy change (ΔS^0) represents the entropy difference of the dye molecules within the substrate [10-12]. In most dyeing processes, the entropy change indicates negative values, because adsorbed dyes stayed inside the substrate molecules are more restrained than dyes in the solution. Therefore, the value of the entropy change could be considered as the measure of immobility of dyes within the substrate [10-12]. Figure 5 shows a linear relationship between $\Delta\mu^0/T$ and $1/T$ for enthalpy change as expected from Eq. (2). From the slope of the straight line, the enthalpy change can be calculated. Meanwhile, from Figure 6 and Eq. (3) showing the linear relationship between $\Delta\mu^0$ and T , the entropy change can be also obtained. The enthalpy and the entropy changes are listed in Table 2. According to Table 2, virgin PET sheet shows higher negative values of ΔH^0 and ΔS^0 , while modified PET with 2 wt% hyperbranched polymer shows lower negative values. The enthalpy change shows the amount of the released heat

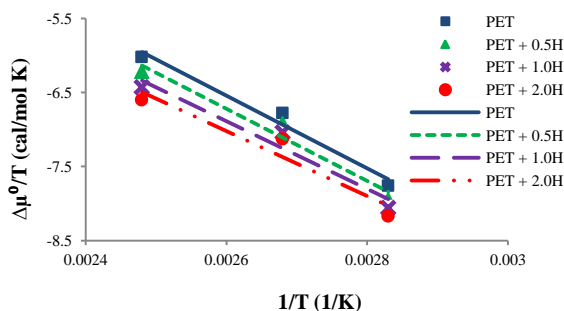


Fig. 5 – Relationship between $\Delta\mu^0/T$ and $1/T$ on enthalpy change

Table 2 – Enthalpy change (ΔH^0) and entropy change (ΔS^0) of C.I. Disperse Blue 56 on virgin and modified PET sheets.

Parameters	PET	PET + 0.5H	PET + 1.0H	PET + 2.0H
ΔH^0 (cal mol ⁻¹)	-4908	-4864	-4570	-4386
ΔS^0 (cal mol ⁻¹ K ⁻¹)	-6.01	-5.69	-4.74	-4.15

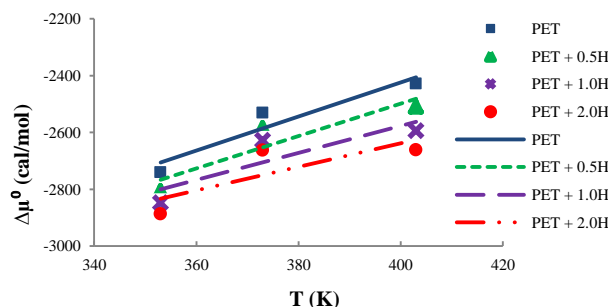


Fig. 6 – Relationship between $\Delta\mu^0$ and T on entropy change

arising from adsorption of dye molecules into polymer chains. The larger negative value indicates that the dye molecules are more strongly embedded within the polymer molecules [10-12]. The entropy change shows the extent of the reduced freedom of dye molecules after the completion of dyeing. The larger negative value of the entropy change represents the fact that the movement of the dye molecules markedly decreases in substrate after dyeing [10-12].

4. CONCLUSION

In this study, thermodynamic parameters of C.I. Disperse Blue 56 on PET sheets modified using a nanostructured hyperbranched polymer were investigated. Atomic force microscopy (AFM) was performed to examine the surface morphology for virgin and modified PET samples. According to the observations made by AFM, dispersion of the hyperbranched polymer in the samples containing 0.5, 1 and 2 wt% hyperbranched polymer was uniform, but some aggregations were observed in sample containing 3 wt% hyperbranched polymer. Finally, dyeing was performed on modified PET including 0.5, 1 and 2 wt% hyperbranched polymer. 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 decreases the glass transition temperature as well as the crystallinity of the modified samples comparing to the virgin PET. The standard affinities of modified PET sheets were higher than those of virgin PET one. In the case of enthalpy and entropy changes, virgin PET sheet showed higher negative values of ΔH^0 and ΔS^0 , while PET with 2 wt% showed the lowest negative values of them.

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REFERENCES

1. E. M. Aizenshtein, *Fibre Chem.* **41**, 1 (2009).
2. H. W. Partridge, *JSDC* **75**, 373 (2008).
3. W. Saus, D. Krittell, E. Schollmeyer, *Text. Res. J.* **63**, 135 (1993).
4. A. Hou, B. Chen, J. Dai, K. Zhang, *J. Clean. Prod.* **18**, 1009 (2010).
5. W. M. Raslan, A. Bendak, E. M. Khalil, T. Fawzi, *Color. Technol.* **126**, 231 (2010).
6. M. Khatibzadeh, M. Mohseni, S. Moradian, *Color. Technol.* **126**, 269 (2010).
7. C. Gao, D. Yan, *Prog. Polym. Sci.* **29**, 183 (2004).
8. K. Inoue, *Prog. Polym. Sci.* **25**, 453 (2000).
9. A. Huit, M. Johansson, E. Malmstrom, *Adv. Polym. Sci.* **143**, 1 (1999).
10. T. K. Kim, Y. A. Son, Y. J. Lim, *Dyes Pigments* **67**, 229 (2005).
11. T. K. Kim, Y. A. Son, Y. J. Lim, *Dyes Pigments* **72**, 246 (2007).
12. G. B. Adebayo, F. A. Adekola, G. A. Olatunji, I. A. Bello, *BPAS* **29**, 77 (2010).