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Dyes and Pigments 58 (2003) 121–125
DYES and PIGMENTS
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Surface modification of PET with ethoxylated hexylaminoanthraquinones by exhaustion method

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Received 23 October 2002; received in revised form 12 January 2003; accepted 11 March 2003

Abstract

Surface modification of poly(ethylene terephthalate) (PET) films by treatment with ethoxylated hexylaminoanthraquinones synthesized by the reaction of 1-aminoanthraquinone with poly(ethylene glycol)s via hexamethylene spacer was investigated. The ethoxylated hexylaminoanthraquinones showed nonionic surfactant nature with definite cloud points, and were successfully applied on to PET by usual exhaustion method as in dyeing. The depth profile of XPS showed that the ethoxylated hexylaminoanthraquinones are adsorbed only onto the extreme surface of PET. Water contact angle was decreased by the adsorption. These results indicate that the ethoxylated hexylaminoanthraquinones anchor on PET surface with ethoxylated hydrophilic moiety outwards.

Keywords: Poly(ethylene terephthalate); Surface modification; Exhaustion; Cloud point; Water contact angle; XPS

1. Introduction

Because of the inherent low reactivity of poly(ethylene terephthalate) (PET) toward chemicals, somewhat complicated processes are adopted for value-added properties of PET in textile finishing; cospinning [1,2], physical coating [3,4], plasma discharge [5–8], alkaline treatment [9–11], and graft polymerisation [12,13], etc. However some of these methods have limited practical use, and are frequently accompanied by the hardening of the touch of PET or elevated production cost. Accordingly there has been great demand for the finishing technology that could be applied to PET fiber more easily and efficiently.

In this study we prepared nonionic surfactant type organic compounds for the surface modification of PET, where the hydrophobic moiety of the compounds could anchor on PET surface and the ethoxylated hydrophilic part orientate outwards, making the surface hydrophilic.

2. Experimental

2.1. Materials

1-Aminoanthraquinone (Aldrich) was recrystallized from ethanol. Poly(ethylene glycol)s (average molecular weight: 600, 1000, 2000 g/mol,

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doi:10.1016/S0143-7208(03)00063-9

Aldrich) were dried by azeotropic distillation with toluene. Tetrahydrofuran (THF) was distilled with sodium. Sodium hydride (Kanto, Japan) was used after removing paraffin oil using hexane. Reagent grade of 1,6-dibromohexane (Aldrich) was used without further purification. Other chemicals were of reagent grade.

PET film (15 μm thickness) (Kolon, Korea) was washed with acetone repeatedly and dried in vacuum.

2.2. Instruments

^{1}H NMR (400 MHz) spectra were recorded on a Bruker Avance 400 spectrometer using tetramethylsilane (TMS) as an internal standard. Chemical shifts are reported in δ units downfield from TMS. UV/vis spectra were recorded on Shimadzu UV 2100 spectrophotometer. Sessile drop contact angle measurements were carried out at 20 °C using a video capture apparatus on Erma Model G-1. XPS surface analysis were performed by using VG ESCALAB 250 with AlK_α (1486.7 eV) radiation for excitation at 15 kV and 10 mA, and an ion gun at 3.0 KV for sputtering (0.93 Å/s) to obtain depth profiles.

2.3. Synthesis of 1-(6-bromohexylamino)anthraquinone

To an ice-cooled 1-aminoanthraquinone (10.00 g, 44.8 mmol) in THF (200 ml) was added sodium hydride (1.29 g, 53.80 mmol) in THF in small portions over 30 min. After 1,6-dibromohexane (43.72 g, 180 mmol) was added to the system, the reaction mixture was refluxed for 20 h. The reaction mixture was filtered and concentrated under reduced pressure. The residual mixture was extracted with hexane to eliminate unreacted 1-aminoanthraquinone. The concentrated extract was subsequently separated by silica gel column chromatography to remove 1,6-dibromohexane (hexane) and to give 1-(6-bromohexylamino)anthraquinone (dichloromethane/hexane mixture) (11.82 g, 68% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.53–1.59 (m, 4H), 1.77–1.81 (m, 2H), 1.90–1.93 (m, 2H), 3.32–3.37 (m, 2H), 3.40–3.45 (m, 2H), 7.05 (d, $J = 8.4$ Hz, 1H), 7.54–7.60 (m, 2H), 7.70–7.76 (m, 2H), 8.23–8.28 (m, 2H), 9.71 (s, 1H).

2.4. Synthesis of 1-(6-ethoxylated hexylamino)-anthraquinones

1-(6-Ethoxylated hexylamino)anthraquinones (EO13-Dye, EO22-Dye, and EO45-Dye) were prepared by the reaction of polyethylene glycols (average molecular weight: 600, 1000, and 2000 g/mol) with 1-(6-bromohexylamino)anthraquinone. To a solution of polyethylene glycol (10.36 mmol) in THF (20 ml) at 60 °C was added sodium hydride (0.32 g, 13.30 mmol) in THF (10 ml) with stirring. After the evolution of hydrogen gas was ceased, 1-(6-bromohexylamino)anthraquinone (4.00 g, 10.36 mmol) in THF (60 ml) was added to the reaction mixture. The reaction mixture was heated at reflux for 15 h and filtered. The filtrate was concentrated under reduced pressure. Unreacted residual 1-(6-bromohexylamino)anthraquinone was eliminated by washing with hexane.

2.5. Cloud point

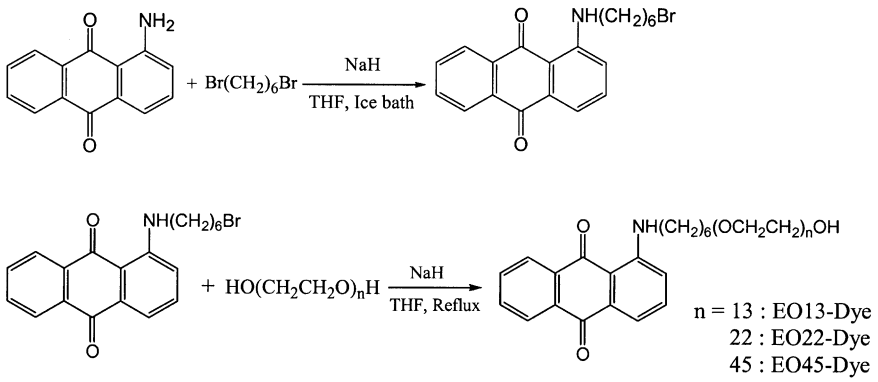
Ten milliliters of 1% aqueous solutions of ethoxylated hexylaminoanthraquinone in a test tube was heated and cooled repeatedly until they became cloudy or clear. The average of the temperature ranges was taken as a cloud point.

2.6. Adsorption isotherms

PET films were dyed with ethoxylated hexylaminoanthraquinones at 130 °C for 10 h under the bath ratio of 5000:1. The dyed films were rinsed with sufficient water, and then extracted with dimethylformamide (DMF). The adsorbed amounts of the compounds were calculated from their absorbance and previously prepared calibration curve.

3. Results and discussion

The synthetic process of ethoxylated hexylaminoanthraquinones is shown in Scheme 1.



Scheme 1. Synthesis of ethoxylated hexylaminoanthraquinone.

Average molecular weights of poly(ethylene glycol)s, 600, 1000, and 2000 g/mol correspond to 13, 22 and 45 repeating ethylene oxide (EO) units approximately. Yields of ethoxylated hexylaminoanthraquinones were 52.6% for EO13-Dye, 51.9% for EO22-Dye, and 48.7% for EO45-Dye. They showed additional multiple signals at 3.57–3.65 ppm in ^{1}H NMR spectra.

Absorption maximums of ethoxylated hexylaminoanthraquinones in DMF were shown at 506 nm, and molar extinction coefficients of EO13-Dye, EO22-Dye, and EO45-Dye were 4950, 3920, and 2310 l/mol cm^{-1} respectively. Although the reddish color of the compounds is disadvantageous for final purpose, we used these colored materials as model compounds for the simplicity of quantitative evaluation.

Adsorption isotherms of ethoxylated hexylaminoanthraquinones on PET films are shown in Fig. 1. Considerable adsorption of ethoxylated hexylaminoanthraquinones occurs although EO13-Dye shows greatest adsorption because of its comparatively low hydrophilicity. However it could be considered that these considerable adsorptions on PET are abnormal because the ethoxylated hexylaminoanthraquinones really resemble usual nonionic surfactants structurally. It is known that nonionic surfactant which has both hydrophobic hydrocarbon part and hydrophilic etheric part in a molecule does not exhaust on PET in aqueous bath. The adsorption of ethoxylated hexylaminoanthraquinones on PET might be due to the characteristics of hydrophobic anthraquinone part. Anthraquinone has good affinity with PET as is used as intermediate in the synthesis of disperse dyes. This affinity leads to the considerable exhaustion although ethoxylated hexylaminoanthraquinones are sufficiently water-soluble.

Nonionic surfactant usually has a cloud point in aqueous solution caused by the dehydration on hydrophilic alkoxy part. Ethoxylated hexylaminoanthraquinones, structurally very similar to nonionic surfactant, also became cloudy in aqueous solution at elevated temperature. The apparent cloud points of the ethoxylated hexylaminoanthraquinones are summarized in Table 1. As is usual, with the length of EO chain the cloud point of ethoxylated hexylaminoanthraquinones

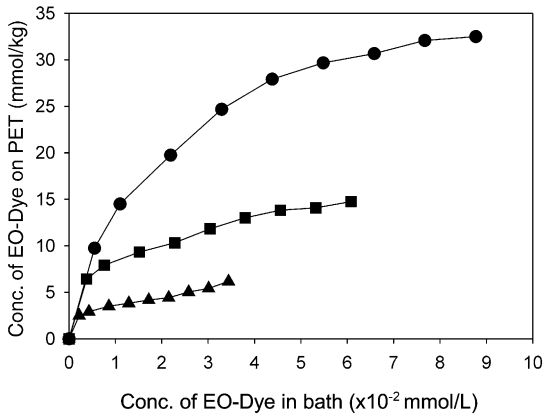


Fig. 1. Adsorption isotherms of EO13-Dye (●), EO22-Dye (■), and EO45-Dye (▲) on PET film at 130 °C.

Table 1
Cloud points of ethoxylated hexylaminoanthraquinones

Hexylaminoanthraquinones	Cloud point (°C)
EO13-Dye	70–75
EO22-Dye	90–95
EO45-Dye	100

increases due to the extensive hydrogen bonding with water molecules. This unique characteristics of inverse solubility with temperature may contribute to the exhaustion of the ethoxylated hexylaminoanthraquinones on PET in aqueous solution: the solubility of the ethoxylated hexylaminoanthraquinones becomes lower at dyeing temperature, 130 °C, and this makes partition of them toward hydrophobic PET, which results in increased adsorption. Accordingly the relatively high adsorption of the ethoxylated hexylaminoanthraquinones on PET shown in the adsorption isotherms could be explained by both their increased partition for PET at the dyeing temperature and the affinity between their anthraquinone moiety and PET.

Although the adsorption of the ethoxylated hexylaminoanthraquinones on PET was durable to thorough washing, the adsorption state is not clear, i.e., the penetration of the ethoxylated hexylaminoanthraquinones into PET is not so probable as to induce even dyeing because of the hydrophilic ethoxylated groups, even though the anthraquinone moiety has sufficient affinity with PET. We carried out surface analysis of the PET films treated with the ethoxylated hexylaminoanthraquinones using XPS. One example is shown in Fig. 2, which shows the XPS depth profiles of oxygen 1s electrons in the PET film treated with EO45-Dye to the concentration of 4.17 mmol/kg-PET. Untreated normal PET has somewhat broad peak due to the carboxylic oxygens of PET at 531.6 and 533.2 eV. On the other hand outermost surface of PET film treated with EO45-Dye shows completely different pattern. This could be explained by that the adsorption of EO45-Dye occurs exclusively on the extreme surface of PET, resulting that ethylene oxide part dominates the surface. To obtain more quantitative information,

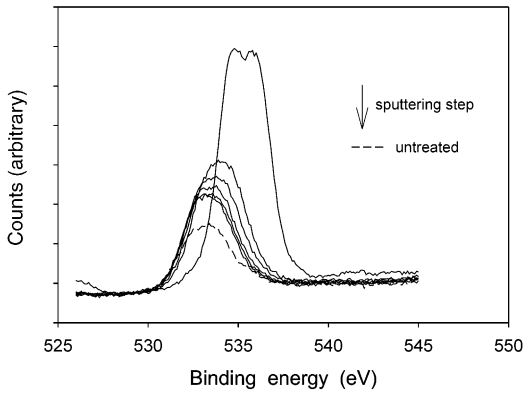


Fig. 2. XPS depth profile for the O 1s electrons in the PET film treated with EO45-Dye.

depth profiles of concentrations of oxygen and carbon are shown in Fig. 3 for the same film as in Fig. 2. It can be seen clearly that within 30 s sputtering time the content of oxygen is high and that of carbon is low compared with untreated normal PET that has constant composition regardless of the scanning depth. Considering that ethoxylated group has relatively high oxygen content compared with PET and that the 30 s sputtering time corresponds to the depth of ca 28 Å, it could be concluded that the adsorbed EO45-Dye does not diffuse into interior of PET but resides in its extreme surface. Additionally the fact that the repeated washing did not reduce the adsorbed amount of EO45-Dye (readily measured from

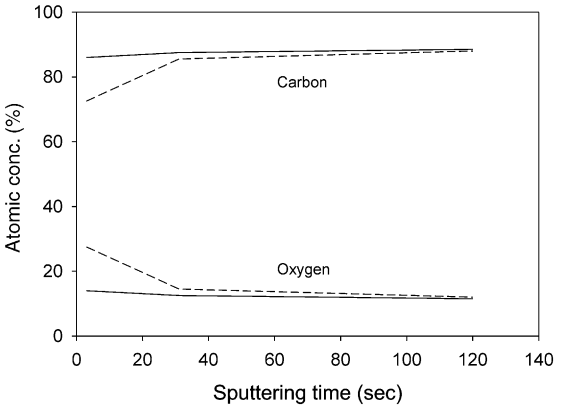


Fig. 3. Depth profile for the concentration of carbon and oxygen in the untreated (solid line) and EO45-Dye-treated (dashed line) PET films.

optical density) on PET film in spite of its sufficient solubility in water means that EO45-Dye anchors on PET surface via anthraquinone moiety with hydrophilic ethoxylated moiety orientating outwards. Although exact picturing of the adsorption state is difficult, it could be expected that the ethoxylated moieties lie down one on another on PET surface if we consider the calculated length of ca. 110 Å for the ethoxylated moiety of an EO45-Dye from molecular model. Similar results were also obtained for EO13-Dye and EO22-Dye.

The adsorption of the ethoxylated hexylaminoanthraquinones on PET surface would change surface properties because of their hydrophilic nature. Water contact angles on the PET films were measured and shown in Fig. 4. It is evident that the adsorption of ethoxylated hexylaminoanthraquinones decreases contact angle and that, at same adsorbed amount, PET film treated with EO45-Dye shows greatest decrease. Low contact angle means that the PET surface has become hydrophilic.

4. Conclusions

Surface modification of PET with water-soluble ethoxylated hexylaminoanthraquinones by exhaustion method was investigated. The adsorption of the ethoxylated hexylaminoanthraquinones on PET is sufficiently durable to washing and, from XPS analysis, it was proved that the adsorption is limited to the extreme PET surface. This adsorption makes the water contact angle decreased, and PET surface very hydrophilic.

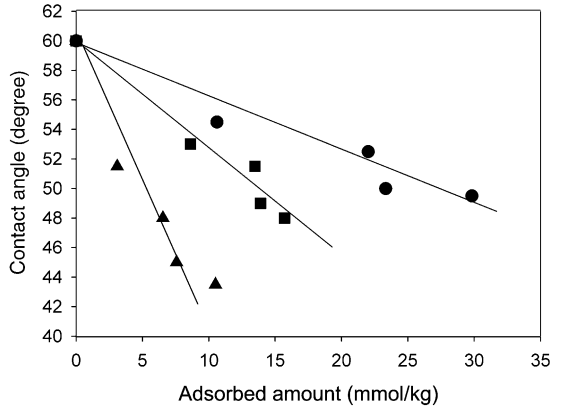


Fig. 4. Water contact angle on PET films treated with EO13-Dye (●), EO22-Dye (■), and EO45-Dye (▲).

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