Improvement of Wettability of Hydrophobic Films by Impregnation of Anthraquinone Attached to Polyoxyethylene Glycol

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ABSTRACT: Amphiphilic anthraquinone bearing polyoxyethylene moiety (PEG_{MW}-AQ) was prepared and impregnated in polyethylene terephthalate (PET) and nylon 6 (ON) films. The uptake of PEG_{MW}-AQ to PET film increased in proportion to the concentration of PEG_{MW}-AQ in a bath, and the contact angle of water dropped on the film decreased with increase in the uptake. At a constant uptake of PEG_{MW}-AQ, the contact angle decreased with an increase of molecular weight of PEG_{MW} attached to the anthraquinone, which indicates that polyoxyethylene moiety of PEG_{MW}-AQ is effective on the wettability of the film. The decrement of water contact angle on PET film dyed with PEG_{MW}-AQ was larger than that on ON film at the same dye uptake because of the higher dyeability of PET film than ON film with PEG_{MW}-AQ. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 545–549, 2005

Key words: dyes; impregnation; polyoxyethylene glycol; films; amphiphiles

INTRODUCTION

Synthetic fibers such as nylon, polyester, and polypropylene are relatively cheap and have stable mechanical properties. They are hydrophobic in nature due to the absence of hydrophilic groups, high crystallinity, and high orientation of polymer chains of the fibers. The hydrophobicity of the synthetic fibers gives properties of low moisture regain and low water retain compared with natural fibers, which produces textiles with uncomfortable handling. It has been reported that chemical and physical modifications of synthetic fibers provide hydrophilicity to hydrophobic fibers with improved handling. Naik et al.[1] and Suzuki et al.[2] found that moisture regain and water retention on nylon or polyester fiber was enhanced by increasing degree of grafting of ethylene oxide or acrylic acid. A laminating hydrophilic polymer on the surface of polyester fabric is also found to improve properties of the fabric relating to moisture regain and wettability.[3,4] Hopen and Schubert[5] and Zhang et al.[6] have reported on the influence of blending polyester or nylon with a hydrophilic substance such as polyoxyethylene glycol on the properties of nylon or polyester fiber. On the other hand, polyoxyethylene glycol derivatives are used as a dispersant of dyestuff, a softener[7] and a swelling agent[8] for textiles. Thus, treatment of synthetic fibers with a disperse dye bearing polyoxyethylene moiety is expected simultaneously to provide hydrophilicity and to color the fiber without dispersant.

In the present study, an anthraquinone dye having a polyoxyethylene chain is prepared and the results of treatment of hydrophobic polyethylene terephthalate and nylon 6 films with the dye derivatives at different times, temperatures, and concentration in a dye bath were reported. The effects of the molecular weight of polyoxyethylene glycol attached to anthraquinone on the wettability of the films were also investigated.

EXPERIMENTAL

Synthesis[9]

1-(Polyoxyethylene glycoxy)anthraquinone (PEG_{MW}-AQ) was prepared according to the modified procedure.[10] 40 mL of tetrahydrofuran (THF) solution containing 1-chloroanthraquinone (1.7 g; 7.0 mmol) was continuously dropped into 10 mL of THF solution containing polyoxyethylene glycol with an average molecular weight of 400 (Nacarai Tesque Co. Ltd.: PEG_{400}) (4.0 g; 10 mmol) and sodium hydrate (0.6 g; 15 mmol) for 4 h. The mixture was stirred and refluxed under a nitrogen gas atmosphere for 5 h. The schematic reaction is shown in Figure 1.

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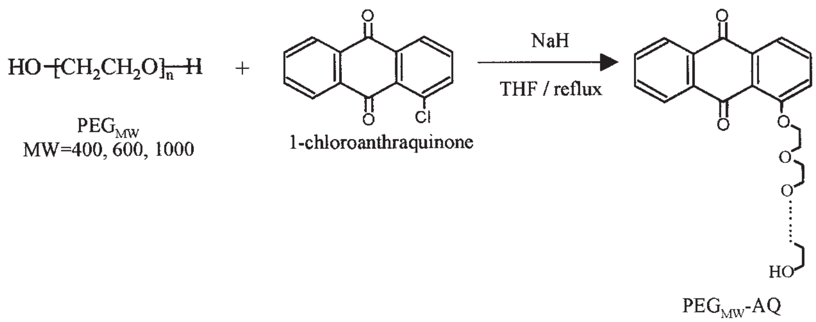

Figure 1 Synthesis of PEG_{MW}-AQ.

The reaction mixture was cooled and concentrated *in vacuo*. The residue was added to 100 mL of distilled water. The precipitate was filtrated and followed by column chromatography (silica gel; Wakogel C-200). The developing solvent was gradually changed from dichloromethane to methanol. Anthraquinone (AQ) having polyethylene glycol with 600 (PEG_{600}) and 1000 of molecular weight (PEG_{1000}) were prepared in a similar manner as described above. PEG_{MW}-AQ was characterized using Time-of-Flight MS (PerSeptive Biosystems Co. Ltd., Voyager MALDI-TOF/MS).

Measurements

Polyethylene terephthalate film (Enblet PET; thickness 12 μm) and nylon 6 film (Enblem ON; thickness 15 μm) were supplied from UNICHIKA Co. Ltd. Both of the films were defatted with an ether Soxhlet extraction unit for 24 h before dyeing. 0.1 g of the film was added to 20 mL of deionized water containing 0.4 m*M* of PEG_{MW}-AQ in a glass bottle with a screw cap. The bottle was set in a thermostated oil bath, shacked at 160 rpm, and kept at a given temperature. After dyeing, the film was sufficiently washed with deionized water, air dried, and kept in a P_2O_5 desiccator. The uptake of PEG_{MW}-AQ to the film was calculated by eq. (1):

$$\text{uptake (\%)} = A_t/A_0 \times 100 \qquad (1)$$

where A_t is the absorbance at a wavelength where a maximum absorbance is obtained (λ_{max}) on the UV/Vis spectrum of PEG_{MW}-AQ extracted from the sample film with 20 mL of formic acid for ON film or hot *m*-cresol for PET film, and A_0 is the absorbance at λ_{max} on the UV/Vis spectrum of PEG_{MW}-AQ in 20 mL of the dye bath. The UV/Vis absorption spectra of PEG_{MW}-AQ were measured by an UV/Vis spectrophtometer (HITACHI U-3210).

The contact angle of distilled water dropped on the sample film was measured with a contact-angle meter (FACE CA-DT).

RESULTS AND DISCUSSION

The UV/Vis adsorption spectra of PEG_{MW}-AQ in methanol, in distilled water, and on PET film are shown in Figure 2.

The spectra of PEG_{MW}-AQ have λ_{max} at 380 nm in methanol while the spectrum of 1-hydroxyanthraquinone (HAQ) bearing no PEG_{MW} chain has λ_{max} at 401 nm. This blue shift from 380 to 401 nm would be due to a solvation of anthraquinone with the PEG_{MW} moiety attached to AQ. In distilled water, λ_{max} of PEG_{MW}-AQ was obtained at 389 nm. The blue shift from 380 nm in methanol to 389 nm in water indicates that PEG_{MW}-AQ slightly aggregates in water. Two shoulder peaks appear at 386 and 420 nm on the spectrum of HAQ, while no more peaks appear on the spectra of PEG_{MW}-AQ in methanol and in water. Both PEG_{MW}-AQ and HAQ adsorbed on PET film, however, show λ_{max} at 408 nm on their UV/Vis spectra accompanied by other two peaks at 430 and 390 nm. This agreement of λ_{max} between PEG_{MW}-AQ and HAQ and the appearance of shoulder peaks of PEG_{MW}-AQ adsorbed on the film suggests no interaction between the PEG moiety and AQ of PEG_{MW}-AQ on PET film. In other words, the PEG moiety would be far apart from the AQ molecule and directed toward the surface of the film.

In Figure 3, the uptake of PEG_{MW}-AQ to PET film and the contact angle of water dropped on the film dyed with PEG_{MW}-AQ are plotted against the dyeing time.

As a control experiment, PET film was dyed with HAQ in the presence of PEG_{MW} and the results are given in Figure 4.

The maximal uptake of PEG_{MW}-AQ to PET film was 14% at the concentration of 0.4 m*M* in the dye bath while that of HAQ was constant at 35% irrespective of the molecular weight of PEG_{MW} added in the dye bath. The decrease of uptake from 35 to 14% suggests that the PEG_{MW} moiety of PEG_{MW}-AQ provides hydrophilicity to AQ, which reduces the distribution of PEG_{MW}-AQ to hydrophobic PET film. However, the uptake of PEG_{MW}-AQ is expected to be enhanced with

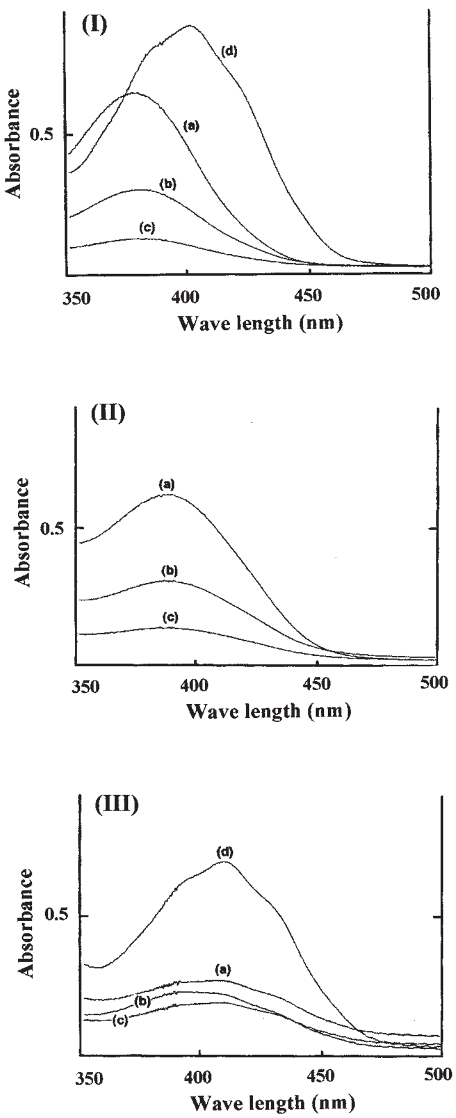

Figure 2 UV/Vis spectra of PEG_{400}-AQ (a), PEG_{600}-AQ (b), PEG_{1000}-AQ (c), and HAQ (d) in methanol (I), distilled water (II), and PET film (III). The solution contained $5\%_{owf}$ of PEG_{MW}-AQ.

an increase in dyeing time because the dye uptake has not reached equilibrium within 120 min (Figure 3).

On the other hand, the contact angle of water dropped on PET film decreased from 75 to 55° at a relatively low uptake of PEG_{MW}-AQ. The contact angles of water on PET film dyed with HAQ in the presence of PEG_{MW} were kept at 75° regardless of the molecular weight of PEG_{MW}. These results suggest that the PEG_{MW} moiety of PEG_{MW}-AQ adsorbed on the film enhances the wettability of PET film, though unmodified PEG_{MW} or HAQ has no effect on the wettability. Thus, the PEG_{MW} moiety was trapped on PET film through adsoption of the AQ portion of PEG_{MW}-AQ and contributes to improvement of the wettability of the film.

Figure 5 gives the correlation between the uptake of PEG_{MW}-AQ to ON film and the dyeing time. The

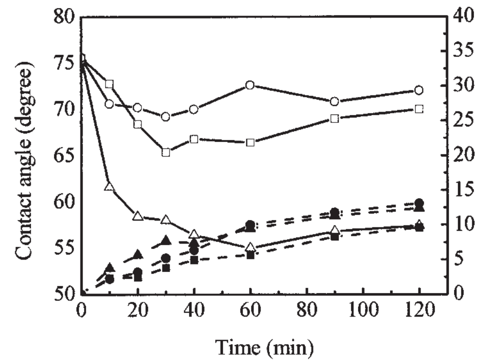

Figure 3 Plots of the contact angle of water on PET film dyed with PEG_{400}-AQ (○), PEG_{600}-AQ (□), and PEG_{1000}-AQ (△) and the uptake of PEG_{400}-AQ (●), PEG_{600}-AQ (■), and PEG_{1000}-AQ (▲) against dyeing time. The film was dyed at 120°C at a liquor ratio of 1 : 200. The dye bath contained 0.4 m*M* of PEG_{MW}-AQ.

contact angle of water dropped on the film dyed with PEG_{MW}-AQ is also plotted against the dyeing time in Figure 5.

The results of control dyeing of ON film with HAQ in the presence of PEG_{MW} are shown in Figure 6.

It is found that the uptake of PEG_{MW}-AQ to ON film is lower than that of HAQ as well as in the case of PET. This decrease of the dye uptake is due to the reduction of hydrophobicity of the dye by modification with PEG_{MW}, which is discussed in the case of PET film. At the same concentration of PEG_{MW}-AQ in a dye bath, the dye uptake to ON film is lower than that of PET film, which leads to a lesser decrease of water contact angle on the ON film. Furthermore, at the same uptake of PEG_{400}-AQ, the decrease of contact angle on ON film was also small compared with that on PET film. It is clear that the wettability of PET film is affected by PEG_{MW}-AQ more than that of ON film because PET film is more hydrophobic than ON film.

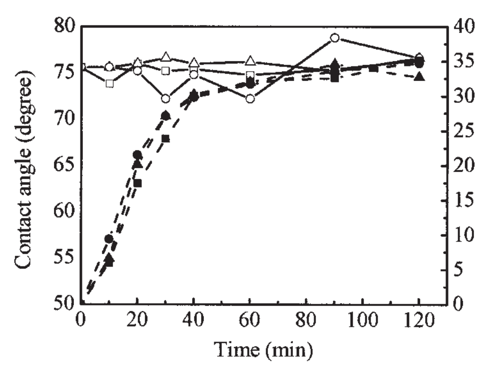

Figure 4 Plots of the contact angle of water on PET film dyed with HAQ in a presence of PEG_{400} (○), PEG_{600} (□), and PEG_{1000} (△) and the uptake of HAQ in a presence of PEG_{400} (●), PEG_{600} (■), and PEG_{1000} (▲) against dyeing time. The film was dyed at 120°C at a liquor ratio of 1 : 200. The dye bath contained 0.4 m*M* of HAQ and PEG_{MW}.

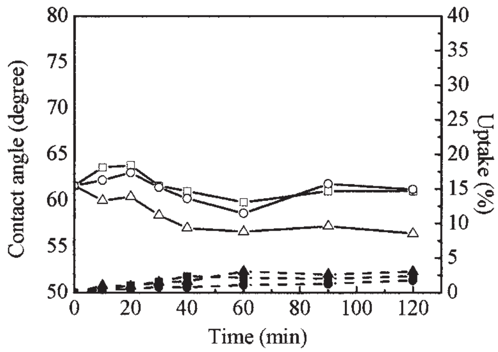

Figure 5 Plots of the contact angle of water on ON film dyed with PEG_{400}-AQ (○), PEG_{600}-AQ (□), and PEG_{1000}-AQ (△) and the uptake of PEG_{400}-AQ (●), PEG_{600}-AQ (■), and PEG_{1000}-AQ (▲) against dyeing time. The film was dyed at 120°C at a liquor ratio of 1 : 200. The dye bath contained 0.4 m*M* of PEG_{MW}-AQ.

Figure 7 shows the relationship between the contact angle of water on the dyed film and the molecular weight of PEG_{MW}-AQ at the constant uptake.

The contact angle of water on the film decreased in proportion to molecular weight, that is, the number of ethylene oxide of PEG_{MW} moiety of PEG_{MW}-AQ. This also indicates that the wettability of PET film is affected by PEG_{MW} moiety of PEG_{MW}-AQ trapped on the film as described in Figures 3 and 4.

The effects of dyeing temperature on the uptake of PEG_{MW}-AQ to PET film and on the contact angle of water on the film are shown in Figure 8.

There is no significant difference between the contact angles of water on the film dyed with PEG_{MW}-AQ at 110 and 120°C. It is expected that the dyeing with PEG_{MW}-AQ even at 110°C provides sufficient enhancement of wettability to PET film.

In Figure 9, the uptake of PEG_{MW}-AQ to PET film and the contact angle of water on the film are plotted against the concentration of PEG_{MW}-AQ in a dyebath.

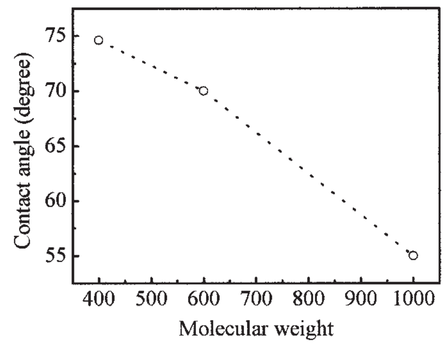

Figure 7 Plot of the contact angle of water on PET film dyed with PEG_{MW}-AQ against the molecular weight of PEG_{MW} attached to AQ. The uptake of PEG_{MW} -AQ was *ca.* 9.5%.

The dye uptake increased with an increase in the concentration of PEG_{MW}-AQ in the dyebath, which enhanced a decrease of water contact angle on the film. The decrement of the water contact angle at the lower uptake of PEG_{MW}-AQ (less than 1%) is larger than that at the higher uptake (more than 1%). The result indicates that even a small amount of PEG_{MW}-AQ effectively improved the wettability of PET film. This could be because introduction of more PEG_{MW}-AQ to the film has little effect on the wettability of the PET film since a large portion of surface of the film is covered with the PEG_{MW} moiety at low uptake of PEG_{MW}-AQ. On the other hand, the dye uptake is larger in the order of PEG_{1000}-AQ > PEG_{400}-AQ > PEG_{600}-AQ at the same concentration of PEG_{MW}-AQ in a dye bath. This order of the dye uptake is essentially the same as the order obtained in Figures 3 and 5. To clarify the reason of the order, more detailed experiments are required.

CONCLUSIONS

Anthraquinone dyes substituted with polyoxyethylene glycol (PEG_{MW}-AQ) have been synthesized and effects

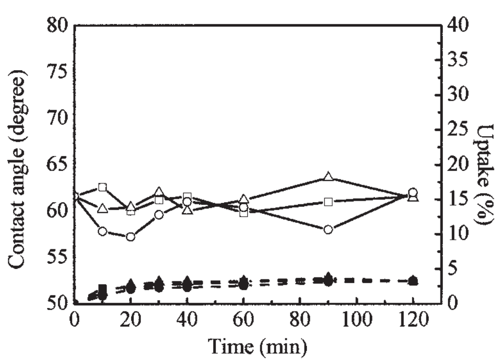

Figure 6 Plots of the contact angle of water on ON film dyed with HAQ in a presence of PEG_{400} (○), PEG_{600} (□), and PEG_{1000} (△) and the uptake of HAQ in a presence of PEG_{400} (●), PEG_{600} (■), and PEG_{1000} (▲) against dyeing time. The film was dyed at 120°C at a liquor ratio of 1 : 200. The dye bath contained 0.4 m*M* of HAQ and PEG_{MW}.

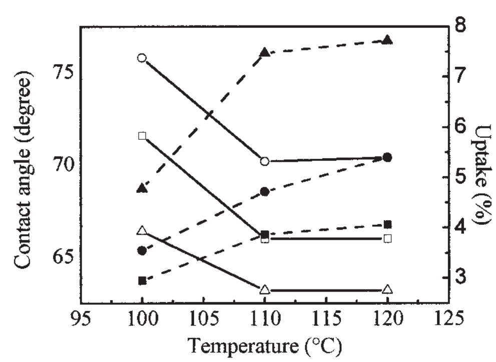

Figure 8 Plots of the contact angle of water on PET film dyed with PEG_{400}-AQ (○), PEG_{600}-AQ (□), and PEG_{1000}-AQ (△) and the uptake of PEG_{400}-AQ (●), PEG_{600}-AQ (■), and PEG_{1000}-AQ (▲) against dyeing temperature. The film was dyed for 120 min at a liquor ratio of 1 : 200. The dye bath contained 0.4 m*M* of PEG_{MW}-AQ.

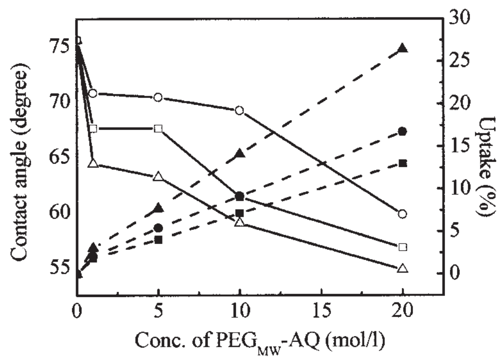

Figure 9 Plots of the contact angle of water on PET film dyed with PEG_{400}-AQ (○), PEG_{600}-AQ (□), and PEG_{1000}-AQ (△) and the uptake of PEG_{400}-AQ (●), PEG_{600}-AQ (■), and PEG_{1000}-AQ (▲) against the concentration of PEG_{MW}-AQ in a dye bath. The film was dyed at 120°C for 120 min at a liquor ratio of 1 : 200.

of PEG_{MW}-AQ trapped onto polyester (PET) and nylon 6 (ON) films on the wettability of the films are investigated by measuring the contact angle of distilled water dropped on the film. The dyeability of PEG_{MW}-AQ on PET film or ON film was smaller than that of hydroxyanthraquinone having no PEG_{MW} chain because the hydrophilicity of the anthraquinone increased with the introduction of PEG_{MW} chain to the dye. However, even at low uptake of PEG_{MW}-AQ, the contact angle of water on the film decreased by dyeing with PEG_{MW}-AQ, which indicates the wettability of hydrophobic films is improved by adsorption of PEG_{MW}-AQ. The uptake of PEG_{MW}-AQ increased with an increase in the concentration of PEG_{MW}-AQ in a dye bath, which caused a proportional decrease of water contact angle. The effect of PEG_{MW}-AQ on PET film as a wetting agent is larger than that on ON film because PET film is more hydrophobic than ON film. The wettability of the film dyed with PEG_{MW}-AQ increased in proportion of the molecular weight of the PEG_{MW} moiety attached to anthraquinone dye. It has been revealed that the PEG_{MW} moiety of PEG_{MW}-AQ contributes to improvement of wettability of more hydrophobic film through the adsorption of PEG_{MW}-AQ to the film.

NOMENCLATURE

Symbol abbreviation	description
AQ	Anthraquinone moiety
PEG_{MW}	Polyethylene glycol with molecular weight of MW
PEG_{MW}-AQ	Polyethylene glycol with molecular weight of MW having anthraquinone moiety
PEG_{400}	Polyethylene glycol with molecular weight of 400
PEG_{600}	Polyethylene glycol with molecular weight of 600
PEG_{1000}	Polyethylene glycol with molecular weight of 1000
PEG_{400}-AQ	Polyethylene glycol with molecular weight of 400 having anthraquinone moiety
PEG_{600}-AQ	Polyethylene glycol with molecular weight of 600 having anthraquinone moiety
PE_{1000}-AQ	Polyethylene glycol with molecular weight of 1000 having anthraquinone moiety
PET	Polyethylene terephthalate film
ON	Nylon 6 film
THF	Tetrahydrofuran
HAQ	1-Hydroxyanthraquinone
A_t	Absorbance at λ_{max} on UV/Vis spectrum of PEG_{MW}-AQ extracted from the sample film with 20 mL of formic acid for ON film or hot *m*-cresol for PET film
A_0	Absorbance at λ_{max} on UV/Vis spectrum of PEG_{MW}-AQ in 20 mL of the dye bath
λ_{max}	Wavelength where maximum absorbance is obtained

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