Fibers and Polymers 2010, Vol.11, No.2, 213-217 DOI 10.1007/s12221-010-0213-7

Union Dyeing of the Photografted PET/Wool Blend Fabrics with Dimethylaminopropyl Methacrylamide

Yuanyuan Dong, Won Seok Lyoo[1], and Jinho Jang*

School of Advanced Materials and System Engineering, Kumoh National Institute of Technology, Kumi 730-702, Korea
[1]School of Textiles, Yeungnam University, Kyonsan 712-749, Korea
(Received July 23, 2009; Revised December 21, 2009; Accepted January 3, 2010)

Abstract: Dimethylaminopropyl methacrylamide (DMAPMA) was grafted onto PET/wool blend fabrics by continuous UV irradiation. Union dyeing of the photografted fabrics was investigated using three reactive dyes of α-bromoacrylamide reactive groups. The influence of grafting yield, DMAPMA concentration, NaCl amount, pH value, and dyeing temperature on the dyeability was evaluated. The dyeability of both PET and wool components was improved significantly by the DMAPMA photografting and successive reactive dyeing. Although the dyeability of the PET component in the blend substantially was improved with higher grafting, equal dyeability between PET and wool was difficult to achieve due to more facile grafting and higher reactivity of the wool component compared with the modified PET component. However, the color fastness of the PET/wool blend fabric was excellent for all three colors. This study may offer a way to achieve union dyeing of PET/wool blend fabrics.

Keywords: PET/wool blend fabric, Photografting, UV irradiation, Dyeability, Reactive dyes

Introduction

Wool is an elastic, hydrophilic, and biodegradable protein fiber which can be dyed readily with various dyes, while it is susceptible to alkaline degradation and shows high felting shrinkage during laundering. PET has outstanding mechanical and physical properties, but its strong hydrophobicity results in low water wettability and limited dyeability to ionic dyes. PET/wool blend fabrics can show the complementary properties compared to pure PET or wool fibers in terms of crease recovery, mechanical strength, abrasion resistance, fast drying, and dimensional stability. The 55:45 PET/wool blend is the minimum polyester content that allows durable pleating of the blend fabric and provides the optimum balance of comfort, wear, and easy-care properties. But in these blends, the production of solid shades using conventional one-bath dyeing methods can be quite difficult. The polyester component is often dyed much weaker in depth than expected [1].

Usually dyeing of PET/wool blend requires two classes of dyes because of the vastly different dyeability of the wool and PET. PET/wool blend is most frequently dyed using disperse dyes for the polyester component and milling acid or 1:2 metal-complex dyes for the wool. Moreover, neutral to slightly acidic conditions are required for both dye classes. However, the disperse dyeing of PET is usually carried out as high as 130 °C under pressure, which may cause severe damage to the wool component. Therefore disperse dyes of low- or intermediate-energy classes are selected to dye the PET at the temperature range of 95-102 °C. If maximum color yield and fastness are essential, high-energy disperse dyes should be applied to the polyester at 130 °C before blending with predyed wool, or adding wool protective agents such as formaldehyde to minimize wool damage. However, the crosslinking action of formaldehyde causes embrittlement of wool, slightly reducing the elongation at break, and markedly lowering the urea-bisulfite solubility [1]. Furthermore, when using sensitive azo disperse dyes, an optimum pH of 5 to 5.5 should be maintained and, if necessary, a reduction inhibitor should be present in the dyebath [2]. Neutral-dyeing of 1:2 metal-complex and milling acid dyes are preferred for the wool component. Most milling acid dyes show satisfactory exhaustion and leveling. Chrome dyes are given an oxidative aftertreatment that can damage the wool and change the hue of the dyed material [3]. The choice between the one-bath and two-bath methods, using disperse and neutrally dyeable acid dyes, depends on depth and fastness requirements. The one-bath method is more economical and gives satisfactory fastness properties in pale or medium depths. The two-bath sequence gives more reproducible solidity or brighter contrast effects as well as optimum fastness in full depths.

Many researchers have also studied on synthesis of the new dyes to dye PET/wool blend fabrics. Radim *et al.* [4] have given disperse azo dyes with two reactive epoxy groups which were synthesized using *N*,*N*-diglycidyl aniline as a coupling component. The dyeing of wool/PET showed high wash fastness but low light fastness. Chao *et al.* [5,6] synthesized several series of dyes containing carboxyl groups such as anthraquinone acid dyes and monoazo disperse dyes with which the dyeability difference of the two fibers for the dying of wool/PET blends can be minimized.

Moreover, photografting of PET with vinyl pyrrolidone (VP) and acryloylmorpholine as monomers also showed an increased dyeability to reactive dyes and increased affinity to various iodine species which imparted antimicrobial

*Corresponding author: jh.jang@kumoh.ac.kr

activity [7]. The photografted PET with (DMAPMA) dimethylaminopropyl methacrylamide showed enhanced dyeability toward the reactive dyes due to the presence of secondary amino groups in DMAPMA. The optimized photografting and dyeing conditions of DMAPMA onto PET were previously reported [8]. DMAPMA containing a secondary amine group was grafted onto PET/wool blend fabrics via UV irradiation and reactive dyes were used to form covalent bonds with both component fibers.

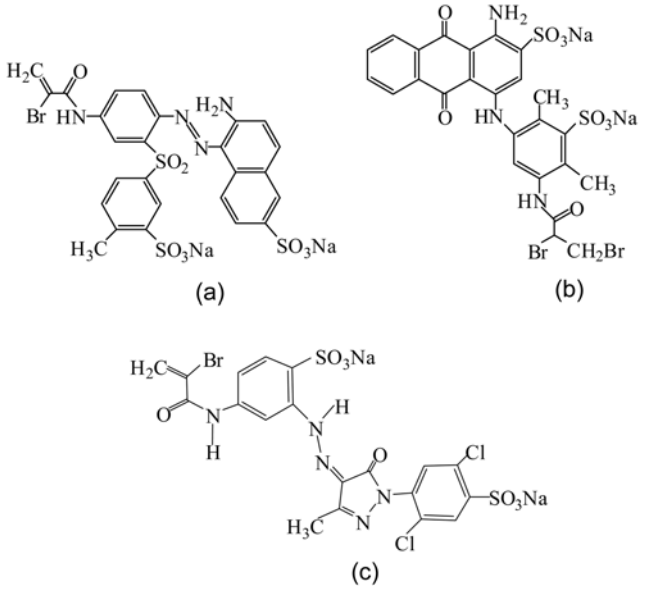
In this study union dyeing of wool/PET blend fabrics was investigated using wool-reactive dyes. The reactive dyes also exert a protective effect on the wool component by reacting with the cystein residues formed by cystine hydrolysis [9].

Experimental

Materials and Chemicals

Woven PET/wool (56/44) blend fabrics of 100 g/m^2 obtained from Cheil Industries, Inc. were used for the study. DMAPMA and benzophenone (BP), supplied by Aldrich Chemical Co., were used as a UV-active monomer and a photoinitiator, respectively [8]. Triton X-100, a wetting agent, was bought from Yakuri Pure Chemical Co. Ltd. (Kyoto Japan). Reactive dyes of Lanasol Red 6G (C.I. Reactive Red 84), Lanasol Blue 3R (C.I. Reactive Blue 50), and Lanasol yellow 4G (C.I. Reactive Yellow 39) were used for dyeing. The chemical structures of dyes are shown in Scheme 1.

Lanasol dyes have been the most successful reactive dyes for wool, because of their high light and wet fastness properties. The reactive groups of the dyes are the α-bromoacrylamido groups which can bond covalently with nucleophilic moieties such as thiols, amines, and alcohols [10].



Scheme 1. Molecular structures of (a) C.I. Reactive Red 84, (b) C.I. Reactive Blue 50, and (c) C.I. Reactive Yellow 39.

Photografting

PET/wool blend fabrics were pretreated by UV apparatus enclosing an H-bulb at UV energy of 10 J/cm^2. Then the blend fabrics were impregnated with a grafting solution containing DMAPMA, BP, and Triton X-100 by subsequently squeezing to 90 % wet pick up. UV irradiation was carried out using a continuous UV irradiator enclosing D-bulb of 80 W/cm^2 intensity. UV energy was controlled by adjusting the speed and passing cycles of a conveyer. After irradiation, the fabrics were thoroughly extracted first with acetone and subsequently with water to remove unreacted monomer, PI, and soluble homopolymer. G and GE represent the grafting yield and grafting efficiency respectively, which were calculated from the following equations:

$$G(\%) = (W_3 - W_1)/W_1 \times 100$$
$$GE(\%) = (W_3 - W_1)/(W_2 - W_1) \times 100$$

where W_1 is weight of original fabric, W_2 and W_3 are weights of the treated fabrics after UV irradiation and after the solvent extraction, respectively.

Reactive Dyeing

The grafted PET/wool fabrics were dyed with red, blue, and yellow reactive dyes. The effect of dyeing conditions on the dyeability were investigated including DMAPMA concentration, dyeing temperature, dyeing time, pH, as well as NaCl addition. After the dyeing process, the dyed fabrics were washed using a Launder-O-meter (ATLAS, Type LP2) first with 2 % detergent solution and subsequently with distilled water at 50 °C, finally with tap water to remove the unfixed dyes on the fabrics. All the dyeings were carried out with 5 % o.w.f. dye using an IR dyeing machine (DL-6000, Starlet Co. Ltd.).

The Assessment of Dyeing Results

A UV/vis spectrophotometer (Agilent Technologies, US/8453) was used for measuring exhaustion (E) based on the remaining dyeing liquor at the maximum absorption wavelength before and after dyeing. K/S was calculated from reflectance at λ_{max} measured with a reflectance spectrophotometer (Gretag Macbeth, Coloreye 3100).

Dye fixation ratio (F), the percentage of the exhausted dye chemically bound on the blend fabric, was calculated by:

$$F(\%) = ((K/S)_b / ((K/S)_a) \times 100$$

where $(K/S)_a$ and $(K/S)_b$ are K/S before and after soaping, respectively.

Total dye fixation (T) of dye exhausted on the blend fabric could be calculated from exhaustion and fixation ratio using:

$$T(\%) = (E \times F)/100$$

The color fastness to laundering and rubbing of dyed fabrics was carried out according to ISO 105-A05 and ISO 10S-X12 with a Launder-O-meter (Atlas, Type LP2) and a crock meter, respectively.

Results and Discussion

Effect of Monomer Concentration on Grafting

Optimization of UV energy is very important for the surface photografting, which primarily depends on the initiation efficiency of photoinitiator and the reactivity of monomers [11,12]. The UV energy was used for all the experiments was 25 J/cm^2 and the BP concentration was 30 % o.w.m. (on the weight of monomer) as determined by the previous study [8]. The grafting yield (G) of the blend fabrics increased with increasing DMAPMA concentration (Figure 1), where the grafting of wool component was much higher than that of PET component. It was attributed to the presence of tertiary hydrogen in wool fiber. The tertiary hydrogen can be abstracted more easily by the benzophenone initiator compared to the secondary hydrogens in PET.

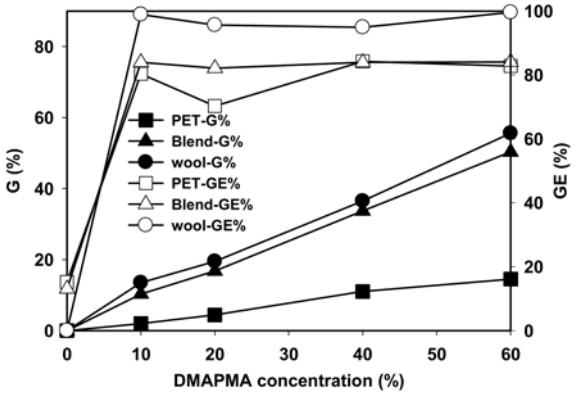


Figure 1. Effect of DMAPMA concentration on grafting yield and grafting efficiency.

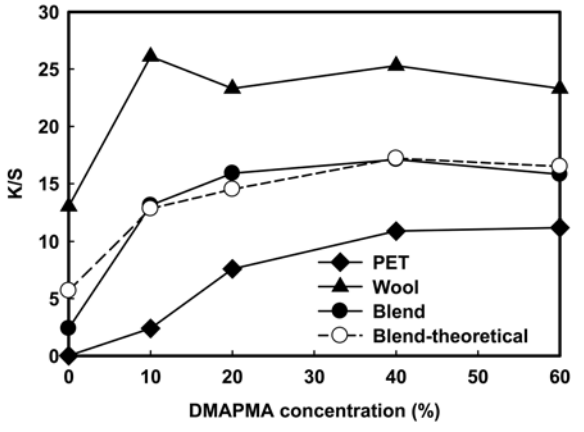


Figure 2. Effect of DMAPMA grafting on *K/S* value (5 %o.w.f., C.I. Reactive Red 84, 50 g/*l* NaCl, pH 7, 60 °C, 90 min).

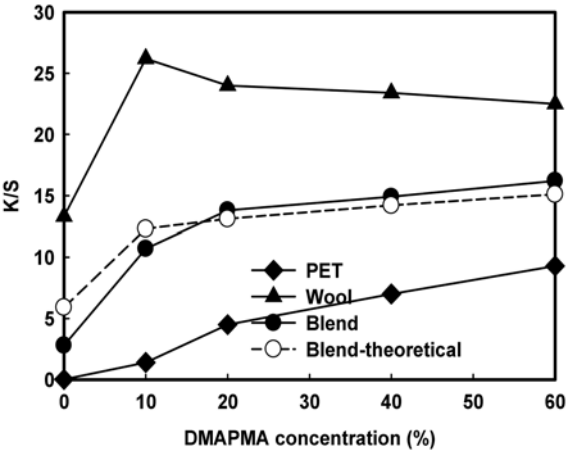


Figure 3. Effect of DMAPMA grafting on *K/S* value (5 %o.w.f., C.I. Reactive Blue 50, 50 g/*l* NaCl, pH 7, 60 °C, 90 min).

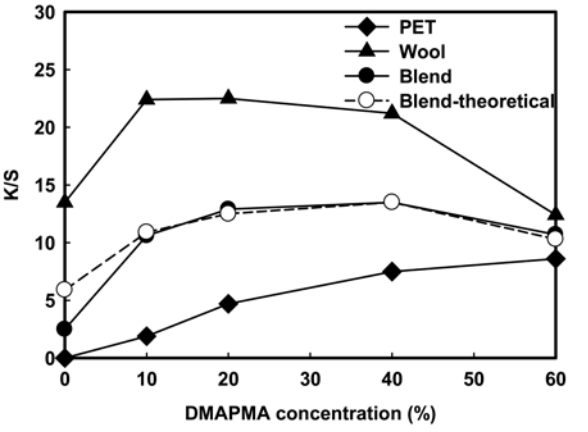
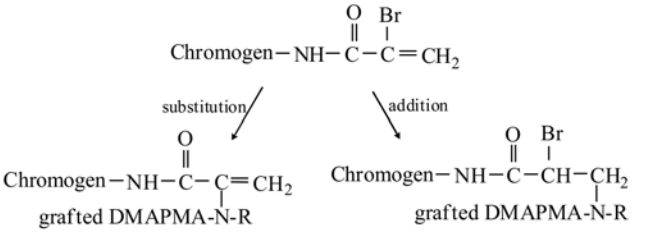


Figure 4. Effect of DMAPMA grafting on *K/S* value (5 %o.w.f., C.I. Reactive Yellow 39, 50 g/*l* NaCl, pH 7, 60 °C, 90 min).



Scheme 2. Reaction mechanism of grafted DMAPMA with wool-reactive dyes (R=-$(CH_2)_3$-N-$(CH_3)_2$).

Effect of DMAPAM Concentration on Dyeability

The dyeability of the grafted PET increased with DMAPMA grafting, while that of the wool component also increased initially, but it decreased with higher grafting of DMAPMA as shown in Figures 2, 3, and 4. As expected, the *K/S* values of the dyed blend fabrics were found to have intermediate values between the pure wool and PET fabrics. The reaction mechanism of the secondary amino groups in the grafted DMAPMA with the α-bromoacrylamido reactive groups of

Table 1. Effect of DMAPMA concentration on dyeability of blend fabrics

Dyes	Agent (%)	*E* (%)	*F* (%)	*T* (%)
Red	0	21.8	92.3	20.1
	10	76.1	89.1	67.8
	20	88.7	82.3	73.1
	40	88.7	85.1	75.5
	60	80.3	87.8	70.5
Blue	0	26.4	90.3	23.8
	10	82.7	94.7	78.3
	20	90.4	84.1	76.0
	40	88.5	89.8	79.4
	60	88.5	90.5	80.1
Yellow	0	19.0	96.2	18.3
	10	71.8	96.4	69.2
	20	77.6	96.3	74.7
	40	71.8	91.8	65.9
	60	60.0	79.3	47.5

the dye molecules was shown in Scheme 2. As more DMAPMA was grafted onto the wool fabric, more dye molecules were exhausted and the total dye fixation increased accordingly (Table 1), resulting from the enhanced zeta potential of the grafted fabrics even though it was not shown. The optimal DMAPMA concentration was 60 % application level because the PET/wool blend fabric showed the lowest *K/S* difference between each component fiber. There was a saturation of exhaustion due to the limited numbers of accessible reactive sites present on the fiber [13]. Following experiments have been carried out to optimize dyeing conditions for the blend fabrics.

Effect of NaCl Addition on Dyeability

Table 2 showed that the sodium chloride addition to the dyebath did not significantly affect the dyeability of the grafted fabrics, although the electrolyte addition was expected to promote dye uptake and accordingly dye fixation on the fabric. The negligible sensitivity of the dyeing to the salt may result from insignificant charge repulsion between the grafted fabrics and the dyes, where the grafting is mainly located at the surface of the fabrics.

Effect of pH Value on Dyeability

Lanasol dyes are normally applied to wool fibers at pH 4.5 to 6.5, because the wool is prone to degrade under alkaline conditions. Higher pH can result in poor exhaustion of dyes and lower pH produce unlevelness due to rapid dye uptake in wool [14]. Considering pH effect on the wool dyeing, optimal dyeing pH was between 5.5 and 7 considering both *K/S* and total dye fixation as shown in Table 3. More acidic environment may hinder the nucleophilic reactions of the reactive groups of the dyes by decreasing nucleophility of the grafted DMAPMA.

Table 2. Effect of NaCl addition on dyeability of blend fabrics

Dyes	Agent (%)	*K/S*	*E* (%)	*F* (%)	*T* (%)
Red	0	15.7	88.9	83.5	74.2
	10	19.8	93.5	95.6	89.4
	30	19.8	88.2	98.5	86.9
	50	17.1	88.7	85.1	75.5
	70	18.8	88.9	94.9	84.4
Blue	0	15.0	96.5	93.8	90.5
	10	15.5	92.7	93.4	86.6
	30	16.4	86.8	98.8	85.8
	50	14.9	88.5	89.8	79.4
	70	16.5	92.2	89.2	82.2
Yellow	0	11.4	87.8	77.0	67.6
	10	11.1	77.5	67.7	54.5
	30	10.1	65.5	78.3	51.3
	50	13.5	71.8	91.8	65.9
	70	15.9	67.1	91.9	61.7

Table 3. Effect of pH on dyeability of blend fabrics

	pH	*K/S*	*E* (%)	*F* (%)	*T* (%)
Red	3	19.1	66.7	85.3	56.9
	5.5	17.8	88.4	91.3	80.7
	7	17.1	88.7	85.1	75.5
	10	16.3	84.9	97.6	82.9
Blue	3	16.7	62.7	79.9	50.1
	5.5	17.5	80.4	98.9	89.4
	7	14.9	88.5	89.8	79.4
	10	16.2	88.0	89.0	78.3
Yellow	3	15.1	72.9	78.2	57.0
	5.5	13.2	69.0	99.2	68.5
	7	13.5	71.8	91.8	65.9
	10	8.4	54.7	76.4	41.8

Table 4. Effect of dyeing temperature on dyeability of blend fabrics

	Temperature (°C)	*K/S*	*E* (%)	*F* (%)	*T* (%)
Red	60	17.1	88.7	85.1	75.5
	80	13.3	73.5	82.6	60.7
	100	16.6	67.6	98.2	66.4
Blue	60	14.9	88.5	89.8	79.4
	80	15.0	71.2	94.9	67.6
	100	14.6	76.9	90.7	69.7
Yellow	60	13.5	71.8	91.8	65.9
	80	13.4	47.0	100.0	47.0
	100	12.4	55.7	87.9	49.0

Table 4 showed that the dyeing of DMAPMA-grafted PET/wool fabrics was little sensitive to temperature change

Table 5. Color fastness properties of blend fabrics

	K/S	Shade	Staining						Rubbing	
			Wool	Acrylic	PET	Nylon	Cotton	Acetate	Dry	Wet
Red	17.1	5	4-5	5	5	4-5	4-5	5	4-5	4-5
Blue	14.9	4.5	5	5	5	5	4	5	4-5	5
Yellow	13.5	4	4-5	5	5	5	4-5	5	4	4-5

between 60 and 100 °C. However, higher temperature dyeing above 100 °C damaged the blend fabric since the wool component was susceptible to thermal degradation. Dyeing results indicated that 60 °C is considered as the appropriate temperature because this dyeing may not require full penetration of dyes into the internal space within the surface-grafted fibers.

Color Fastness to Laundering and Rubbing

As shown in Table 5, the fastness to washing and rubbing is excellent to good. The good color fastness of the grafted PET fabrics again verified the formation of covalent bond between the grafted chain and the dye molecules in spite of the presence of surface grafting of DMAPMA on the fibers.

Conclusion

DMAPMA was easily grafted onto the PET/wool fabrics by continuous UV irradiation under ambient condition. The dyeability of PET/wool blend fabrics to wool reactive dyes improved by the photografting of DMAPMA. With increasing DMAPMA application, proportional increase in the grafting yield of both component fibers was observed, where grafting yield onto wool was higher than that onto PET. The *K/S* value for the grafted fabrics increased remarkably due to the formation of covalent bonds between secondary amine groups in the grafted polymer and reactive groups in the dye molecules. And in order to protect the wool component in the PET/wool blend fabric, the dyeing should be carried out under neutral condition at low temperature of 60 °C. The color fastness to washing and rubbing of the grafted PET/wool blend fabric were excellent to good in spite of apparent surface grafting.

Acknowledgement

This work was supported by grant No. RTI04-01-04 from the Regional Technology Innovation Program of the Ministry of Commerce, Industry, and Energy (MOCIE).

References

1. J. Shore, “Blends Dyeing”, pp.138-148, Society of Dyers and Colourists, Manchester, 1998.
2. P. Rube and D. Wegerle, *Melliand Textilber*, **57**, 496 (1976).
3. T. Balchin, *Am. Dyest. Rep.*, **72**, 27 (1983).
4. R. Hrdina, S. Lunak Jr, and L. Burgert, *Dyes Pigm.*, **37**, 71 (1998).
5. Y. C. Chao and M. Lin, *Dyes Pigm.*, **37**, 357 (1998).
6. Y. C. Chao and M. Lin, *Dyes Pigm.*, **44**, 209 (2000).
7. W. Huang and J. Jang, *J. Korean Soc. Dyers Finishers*, **20**, 28 (2008).
8. W. Huang and J. Jang, *J. Korean Soc. Dyers Finishers*, **21**, 40 (2009).
9. D. M. Lewis, *Rev. Prog. Color.*, **19**, 49 (1989).
10. D. M. Lewis, “Wool dyeing”, pp.225-226, Society of Dyers and Colourists, Bradford, 1992.
11. K. Studera, C. Decker, E. Beck, and R. Schwalm, *Prog. Org. Coat.*, **48**, 92 (2003).
12. K. Studer, C. Decker, E. Beck, and R. Schwalm, *Prog. Org. Coat.*, **48**, 101 (2003).
13. R. M. El-Shishtawy, Y. A. Lyoussef, N. S. E. Ahmed, and A. A. Mousa, *Dyes Pigm.*, **72**, 57 (2007).
14. R. M. Christie, R. R. Mather, and R. H. Wardman, “The Chemistry of Colour Application”, pp.107-108, Blackwell Science, Oxford, 2000.