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〈Research Paper〉

Reactive-dyeable Treatment of PET Fabrics via Photografting of Dimethylaminopropyl methacrylamide

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Abstract— Dimethylaminopropyl methacryamide was photografted onto PET fabrics by continuous UV irradiation under ambient conditions. Several factors affecting the photografting were studied including irradiation energy, monomer and photoinitiator concentrations. ATR and ESCA analysis showed the successful grafting of the monomer onto the PET surface. The grafted PET fabrics showed higher zeta potentials below pH 7 compared with the ungrafted PET. The dyeability of the grafted PET fabrics to two α-bromoacrylamide reactive dyes was investigated under various dyeing conditions including dye concentration, pH, dyeing temperature and time. The grafting imparted the reactive dyeability to PET fabrics, which was proportional to the grafted monomer content. The reactive dyeing behavior of the grafted PET fabrics was similar to that of conventional wool fabrics.

Keywords: *PET fabric, photografting, UV irradiation, dyeability, wool, reactive dyes*

1. Introduction

PET fiber is one of the most widely used synthetic fibers in the textile industry due to its good mechanical and chemical properties. However, the hydrophobicity and low dyeability have always been problems for use in wider applications. For example, PET and wool blended fabrics can give improved resistance to wear and creasing.

However, the dyeing of PET is usually carried out with disperse dyes at temperatures as high as 130℃ under pressure. This usually causes damages of the wool component. Moreover, disperse dyes cover a wide range of colors with few brilliant shades[1]. Acid, chrome, metal-complex and reactive dyes are the main classes used for dyeing wool among which the metal-free reactive dye is one of the environmentally friendly dyes. Also it has an excellent colorfastness property as well as a bright shade[2]. The reactivity of Lanasol dyes is associated with the α-bromoacrylamido group which can bond covalently with nucleophilic moieties such as thiols, amines and alcohols. The reaction of these dyes proceed via either nucleophilic substitution of the bromine atom or 1,4-Michael addition across the double bond of the α-bromo-acrylamido group with certain amino acid side chains of wool protein. Regardless of the pathway involved, the intermediates can cyclise to form an aziridine ring and crosslink wool protein[3].

A great amount of research has been done on improving the dyeability of PET with either the modification of PET or the synthesis of new dyes. Cationic dyeable treatment of PET by continuous UV/O_3 irradiation was examined in our previous studies[4,5]. *Kim et al.* which synthesized the reactive disperse dye carrying actoxyethylsulphone group and applied it to PET and nylon fabrics to improve their dyeability and color fastness[6]. The dyeing of PET film and PET knitted fabrics using a supercritical CO_2 medium with anthraquinone and azo dyes was studied by *Santos et al.*[7] Grafting

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functional monomers onto synthetic fiber, fabric or film is one of the effective ways for improving its inherent deficiency such as low dyeablility. The grafting copolymerization can be induced by EB, UV irradiation, ionizing radiation, or wet thermal treatments. Many researchers have studied the introduction of functional groups such as carboxylic acid, hydroxy, or amide onto PET using various methods[8-14].

Little study is reported on surface photografting of PET fabric to improve its dyeability to reactive dyes. The present study is to impart PET fabric reactive dyeability by grafting of dimethylaminopropyl methacrylamide (DMAPMA) containing a secondary amino group via a continuous surface photografting process. Continuous surface photografting is an effective way to introduce functional groups on various substrates because of rapid and efficient grafting with conventional padding and UV irradiation, absence of organic solvent, environmental friendliness, and low energy consumption as explained in previous study[15]. Surface modification may be a step forward to accomplish ‘universal dyeing’ so that all kinds of fibers can be colored by a class of dyes.

The characterization of the grafted PET fabrics with DMAPMA was carried out by ATR and ESCA analysis. Surface zeta potentials of the grafted fabrics were also measured.

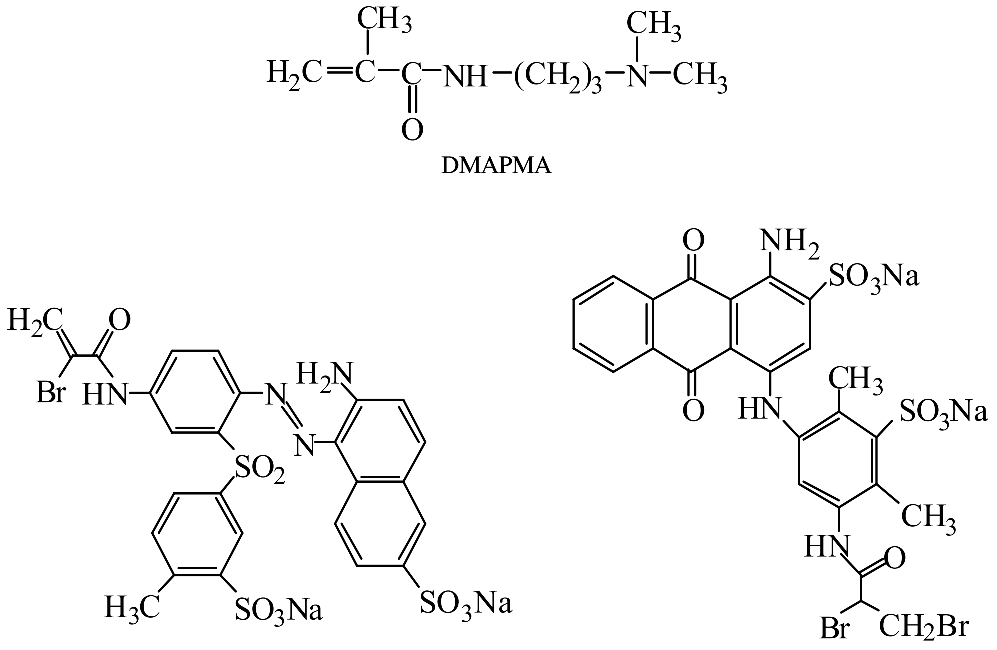
The dyeing behavior of the grafted PET fabrics to Lanasol dyes was investigated. This included the effect of grafting, dye concentration, pH, dyeing temperature and time.

2. Experimental

2.1 Materials and chemicals

Plain weave PET(77g/m^2) and wool(107g/m^2) fabrics were used for the grafting substrate. Supplied by Aldrich Chemical Co., N-[3-(Dimethylamino)propyl] methacrylamide (DMAPMA) and benzophenone (BP) were used as a monomer and a hydrogen-abstractable photoinitiator respectively. Triton X100, a wetting agent, was bought from Yakuri Pure Chemical Co. Ltd (Kyoto Japan). Reactive dyes of Lanasol Red 6G (C.I. Reactive Red 84) and Lanasol Blue 3R (C.I. Reactive Blue 50) were used for dyeing.

The chemical structures of DMAPMA and dyes are shown in Fig. 1.



$$H_2C{=}\overset{\displaystyle CH_3}{\overset{|}{C}}-\underset{\underset{\displaystyle O}{\|}}{C}-NH-(CH_2)_3-\overset{\displaystyle CH_3}{\overset{|}{N}}-CH_3$$

DMAPMA

C.I. Reactive Red 84

C.I. Reactive Blue 50

Fig. 1. Molecular structures of DMAPMA and reactive dyes.

2.2 Photografting

PET fabrics were immersed into the grafting formulation containing monomer, PI and Triton X100. Then the wetted fabric was squeezed at a wet pick up of about 60% using a padding mangle. A UV apparatus enclosing a D-bulb (a metal doped mercury lamp) of 80W/cm intensity was used for UV irradiation. UV energy was controlled by adjusting the speed and passing cycles of a conveyor belt. After irradiation, the fabrics were thoroughly extracted 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 the weight of the original fabric, W_2 is the weight of fabric after UV irradiation, and W_3 is the weight of fabric after the solvent extraction.

2.3 Surface analysis

A Jasco FT-IR 300E spectrophotometer was used for the functional group analysis of the UV-cured monomers in this study. The samples were blended with KBr and made into discs for the measurement. The infrared absorbance of the grafted PET fabrics was measured by ATR apparatus attached to a ZnSe crystal using a Tensor 27 spectrophotometer (Bruker Optics). ESCA (Electron Spectroscopy for Chmical Analysis) was performed on the surface of grafted PET fabrics using a Quantera SXM spectrophotometer (ULVAC-PHI). The element ratio of O_{1s} or N_{1s} to C_{1s} was calculated.

2.4 Zeta potential measurement and reactive dyeing

Surface zeta potentials of the grafted PET fabrics were measured using electrophoretic light scattering spectrophotometer (ELS-300, OTSUKA, Japan). The measurement was carried out with 10mM NaCl electrolyte at the pH region of 3 to 10.

The grafted PET and wool fabrics were dyed with the reactive red and blue dyes. The dyeing were carried out using a IR dyeing machine (DL-6000, Starlet Co. Ltd.).

The standard dyeing conditions were 5%owf dye concentration with 50g/L NaCl at 60℃ and pH 7 for 90 min unless mentioned otherwise. Furthermore, the effects of dye concentration, pH, dyeing temperature and time were investigated. After the dyeing, the dyed fabrics were washed to remove the unfixed dyes on the fabrics first with 2 wt % detergent solution (ECE Phosphate REF DET B) and subsequently with distilled water at 50℃ for 30 minutes respectively.

The colorfastness to laundering and rubbing of the dyed fabrics was determined according to ISO 105-CO2 and ISO 105-X12 using a Launder-O-meter (Atlas, Type LP2) and a crock meter respectively.

3. Results and discussion

3.1 Grafting yield (G%) and Grafting efficiency (GE%)

The benzophenone can abstract hydrogen from PET molecules upon UV irradiation and the polymer radicals initiate the graft copolymerization of DMAPMA monomer, which is expected to reduce the fast inhibition reaction of atmospheric oxygen due to the presence of a nitrogen atom in the molecular structure. The effects of UV energy and monomer concentration on the DMAPMA grafting were shown in Fig. 2. G% increased with the increase in monomer concentration because rate of polymerization is proportional to the monomer content applied on the fabric. However, GE% slightly decreased with increasing monomer concentration probably due to the inevitable homopolymerization of the monomer. A higher UV energy was beneficial for efficient grafting because sufficient UV energy is required to excite the benzophenones to initiate polymer radicals via hydrogen abstraction. Table 1 showed the effect of

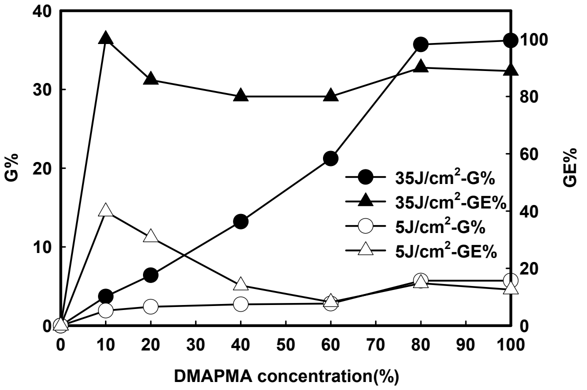


Fig. 2. Effect of monomer concentration and UV energy on DMAPMA grafting (BP 30%owm).

Table 1. Effect of BP concentration on DMAPMA grafting (DMAPMA 20%, UV energy 25J/cm^2)

BP (%owm)	G%	GE%
0	2.1	67.2
5	3.5	61.7
10	4.1	64.4
20	4.8	66.5
30	6.4	71.5
40	6.5	74.4

BP concentration on the grafting[16]. Both G% and GE% increased apparently with increasing BP concentration. However, a photoinitiator concentration higher than 30% of the weight of monomer may encourage the termination reactions of the initiated and propagating radicals.

3.2 Surface analysis

IR spectrum of UV-cured DMAPMA was shown in Fig. 3(a). With N-H stretching located at 3391cm^{-1}, the secondary amide carbonyl stretching and N-H bending bands of the poly DMAPMA appeared at 1645cm^{-1} and 1537cm^{-1} respectively. The DMAPMA-grafted PET fabric(Fig. 3(c)) also showed strong absorption bands at 3413cm^{-1} and 1639cm^{-1} assigned to the stretching vibrations of the amide linkage in the grafted fabric.

The subtracted spectrum(Fig. 3(d)) indicated the presence of the graft DMAPMA on the surface of PET fabric, where the amide vibrations were observed at 3415cm^{-1}, 1639cm^{-1} and 1537cm^{-1}.

The surface of the grafted PET fabrics was also investigated by ESCA analysis(Table 2).

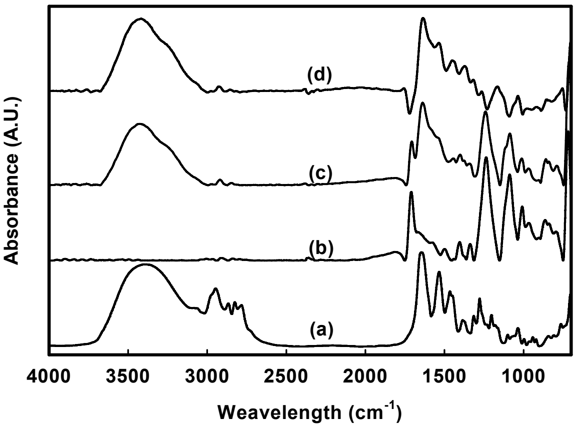


Fig. 3. IR spectra of (a) photopolymerized DMAPMA, (b) PET, (c) grafted PET (5.7%G) and (d) subtraction of (c) with (b).

Table 2. Atomic compositions of untreated and grafted PET fabrics

Grafting (%)	C_{1s} (%)	O_{1s} (%)	N_{1s} (%)	O_{1s}/C_{1s} (%)	N_{1s}/C_{1s} (%)
Untreated	75.4	23.4	1.1	31.0	1.5
6.4	86.6	6.5	6.9	7.5	8.0
21.2	75.5	12.7	11.8	16.8	15.6

Carbon content in the outer surface of PET fabrics increased with grafting, while oxygen content decreased. The increase in N_{1s} peak at the binding energy of 399eV substantiated the presence of nitrogen on the surface of the grafted PET. The atom ratio of N_{1s}/C_{1s} increased with the increase in grafting yield accordingly.

3.3 Surface zeta potentials

It can be seen from Fig. 4 that the surface zeta potentials of the grafted PET fabrics were higher than that of the untreated fabrics below pH 7. The protons in the mediummay complex with the introduced secondary or tertiary amines in the grafted PET fabrics resulting in elevating zeta potentials to a weak positive charge. However, the grafted PET fabric gave a lower zeta potential in the higher pH region than the untreated one, possibly because of the higher polarity of amide and tertiary amino groups in the grafted poly DMAPMA compared to the relatively nonpolar surface of PET.

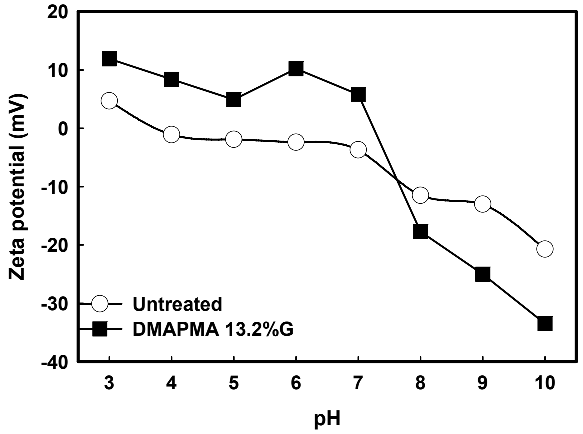


Fig. 4. Zeta potentials of grafted PET fabrics.

3.4 Dyeability to reactive dyes

The effect of grafting on the reactive dyeing was investigated as shown in Fig. 5. It can be seen that both the K/S and the exhaustion of the grafted PET fabrics remarkably increased with increasing grafting yield. Maximum color yields and exhaustion were obtained at 21.2%G for both dyes. While pristine PET fabrics showed no appreciable dyeability, a deep shade was obtained with the grafted PET in both dyes indicating the covalent bond formation between the secondary amino groups of the grafted DMAPMA and the dyes. Dyeing mechanism may follow the reaction mechanism of the α-bromoacrylamido reactive dyes with amine-containing amino acid residues in wool as shown in Fig. 6.

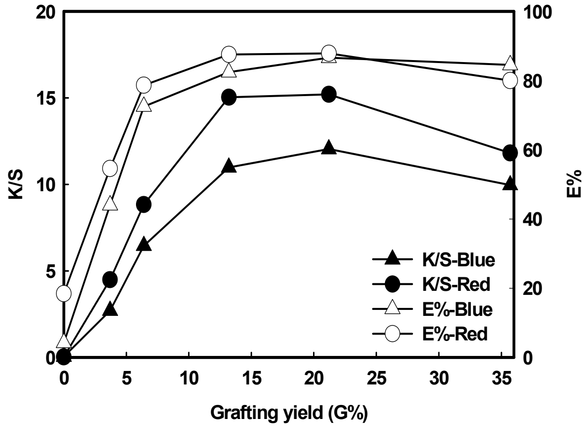


Fig. 5. Effect of DMAPMA grafting on color yield and exhaustion.

The effect of dye concentration on the build-up properties of DMAPMA-grafted PET fabrics was shown in Fig. 7. As a comparison, wool fabrics were also dyed with the same dyes under the same dyeing condition. While ungrafted PET fabrics showed no coloration even with higher dye concentration, the color yields of the grafted fabrics reached 10 or higher when 5.7% grafted fabrics were dyed with 5%owf of both dyes. Surprisingly wool fabrics exhibited similar dyeability to the dyes compared to that of the grafted PET fabrics at the dye concentration of 3%owf or less. Considering pH influence on the dyeability, optimum dyeing was obtained at pH 7 as shown in Fig. 8.

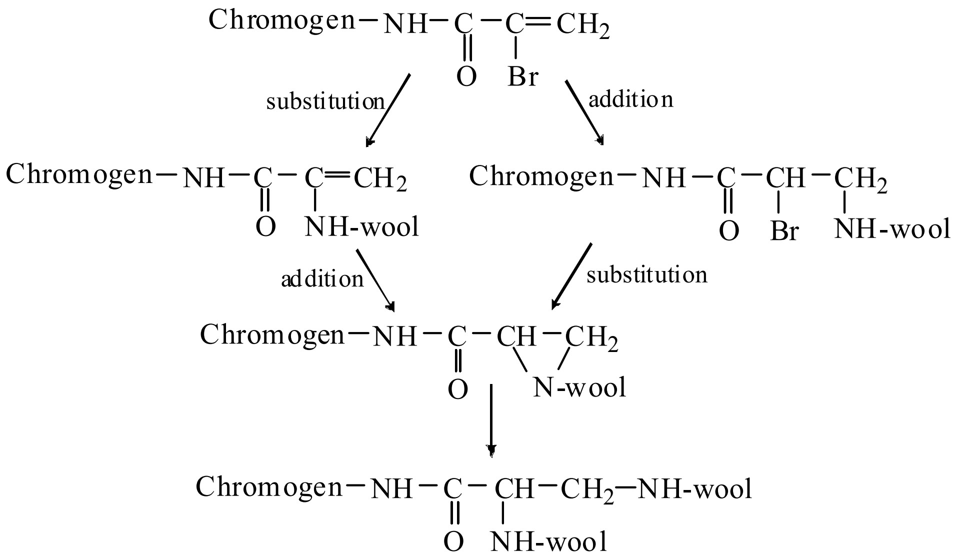
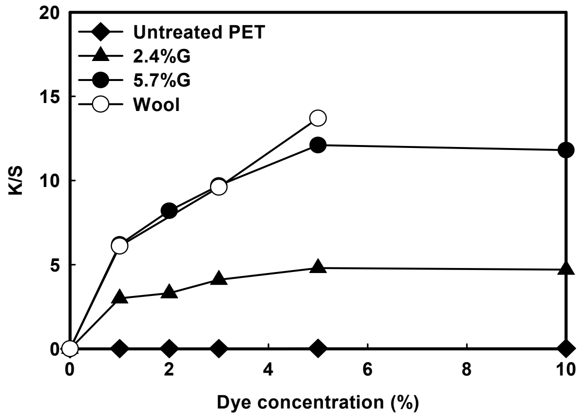
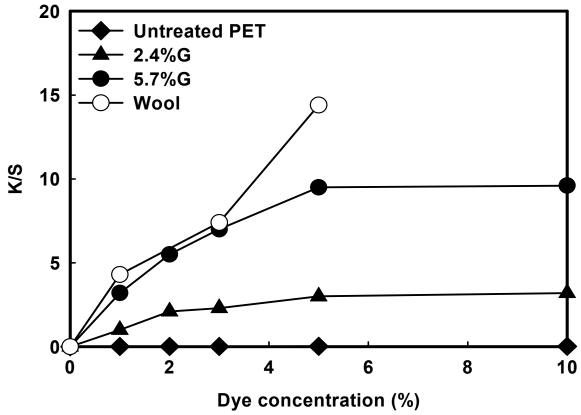


Fig. 6. Reaction mechanism of α-bromoacrylamide dyes with wool residue[3].



(a) C.I. Reactive Red 84



(b) C.I. Reactive Blue 50

Fig. 7. Effect of dye concentration on K/S of wool and grafted PET fabrics.

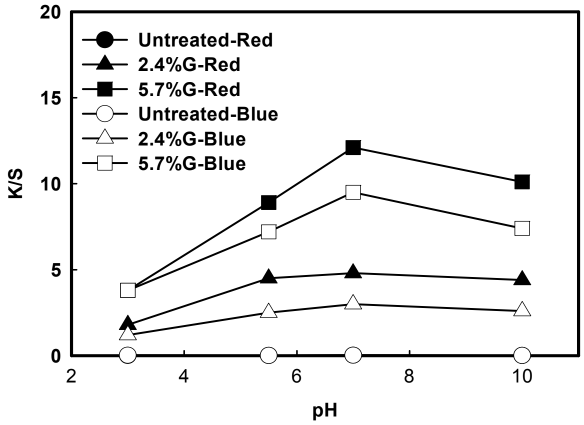


Fig. 8. Effect of pH value on K/S of grafted PET fabrics.

It indicated a higher reactivity of secondary amino groups of the grafted DMAPMA under the neutral pH environment. Both acidic and alkaline environment may hinder the nucleophilic substitution and/or Michael addition of the reactive groups of the dyes by decreasing nucleophilicity of the DMAPMA or potential hydrolysis of the amide linkage.

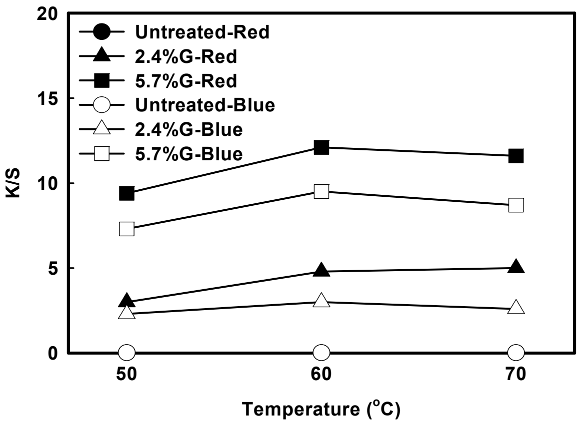


Fig. 9. Effect of dyeing temperature on K/S of grafted PET fabrics.

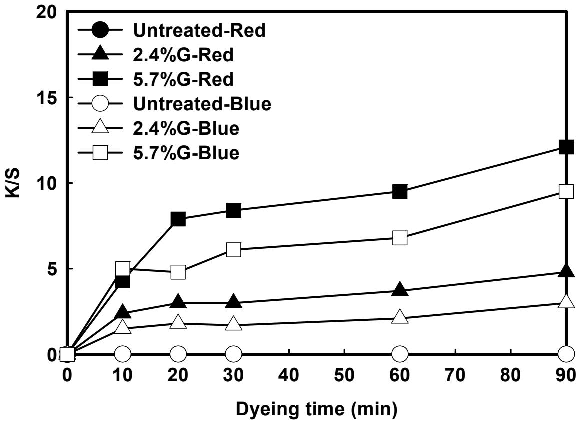


Fig. 10. Effect of dyeing time on K/S of grafted PET fabrics.

Neutral dyeing of DMAPMA-grafted PET fabrics was less sensitive to temperature change in the regions of 50℃ to 70℃(Fig. 9). The K/S values increased slightly to 60℃ and remained similar at 70℃. Color yield showed significant increase at the dyeing time of 20 min even though prolonged dyeing. Increased dyeing time was beneficial due to a gradual increase in K/S and good leveling properties (Fig. 10). Therefore, the reactive dyeing of DMAPMA-grafted PET fabrics can be achieved at conventional reactive dyeing conditions. The color fastness properties to washing were good to excellent for all the grafted fabrics(Table 3), again substantiating the formation of covalent bonds between the grafted poly DMAPMA and the dye molecules. Unsurprisingly colorfastness of the ungrafted PET fabric was excellent resulting from its negligible dyeability.

Table 3. The colorfastness of untreated and grafted PET fabrics

Dyes	G%	K/S	Shade	Staining						Rubbing	
				Wool	Acryl	PET	Nylon	Cotton	Acetate	Dry	Wet
Reactive Red 84	0	0.0	4	4-5	5	5	4-5	4-5	5	5	5
	3.7	4.5	4.5	4-5	4-5	4-5	3-4	4	4-5	4	3
	6.4	8.8	4.5	4	4-5	4-5	3-4	3-4	4-5	4-5	3
	13.2	15.0	3	4-5	4-5	4-5	4	4	4-5	4	2-3
	21.2	15.2	4	4-5	4-5	4-5	3-4	4	4-5	4	2-3
	35.7	11.8	3	4-5	4-5	4-5	4	4	4-5	4	2-3
Reactive Blue 50	0	0.0	4.5	4-5	5	5	4-5	4-5	5	5	5
	3.7	2.7	3.5	4	4-5	4-5	4	4	4-5	3-4	3-4
	6.4	6.5	4	3-4	4-5	4-5	4	4	4-5	4	3
	13.2	11.0	4	4-5	4-5	4-5	4	4-5	4-5	4	2-3
	21.2	12.0	4.5	3-4	4-5	4	4	4-5	4-5	4-5	2-3
	35.7	10.0	4	4	4-5	4-5	3-4	4	4-5	4	2-3

As expected from conventional reactive dyeing, both shade change and stain rating were good to high for both colors. However, the colorfastness to wet rubbing was rated slightly lower than that of dry rubbing in the cases of deep-dyed fabrics, indicating that proper neutralization step with ammonia or hexamethylene tetramine should be employed to obtain high wet fastness[3].

4. Conclusions

In this study, PET fabrics were photografted with DMAPMA containing a secondary amino group. ATR and ESCA analysis proved that the DMAPMA polymer was grafted on the surface of PET. The grafted PET fabrics became reactive dyeable. The dyeing of the grafted PET fabric can be successfully achieved at a low temperature of 60℃ under a neutral pH environment which is similar to conventional dyeing condition. The color fastness of the dyed fabric was excellent. The grafting of DMAPMA onto PET is expected to be applied to the wool/PET blended fabrics so that an one-bath union dyeing of wool/PET blend may be possible without the damages of the wool component.

Acknowledgement

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References

1. R. M. Christie, R. R. Mather, and R. H. Wardman, "The Chemistry of Colour Application", Oxford, Blackwell Science Ltd, 2000.
2. J. Park, and J. Shore, "Practical Dyeing", Bradford, Society of Dyers and Colourists, 2005.
3. D. M. Lewis, "Wool Dyeing", Bradford, Society of Dyers and Colourists, 1992.
4. J. Jang, M. Kim, and Y. Jeong, Cationic Dyeable Treatment of PET and PTT Fabrics by Continuous UV/O_3 Irradiation, *Textile Science and Engineering*, **40**, 424-430(2003).
5. J. A. Son and J. Jang, Tone-on-tone Dyeing of PET Fabrics using Selective UV Irradiation and Cationic Dyes, *Textile Science and Engineering,* **44**, 142-148(2007).
6. J. S. Bae, K. S. Kim, J. H. Park, and S. D. Kim, Dyeing Properties of a Reactive Disperse

Dye carrying Acetoxyethylsulphone Group, *Dyes and Pigments*, **75**, 170-175(2007).

7. W. L. F. Santos, A. P. Moura, N. P. Povh, E. C. Muniz, and A. F. Rubira, Anthraquinone and Azo Dyes in Dyeing Processes of PET Films and PET Knitted Fabrics using Supercritical CO_2 Medium, *Macromolecular Symposia*, **229**, 150-159(2005).
8. E. Uchida, H. Iwata, and Y. Ikada, Surface Structure of Poly(ethylene terephthalate) Film Grafted with Poly(methacrylic acid), *Polymer*, **41**, 3609-3614(2000).
9. C. He and Z. Gu, Studies on Acrylic Acid-grafted Polyester Fabrics by Electron Beam Preirradiation Method. I, Effects of Process Parameters on Graft Ratio and Characterization of Grafting Products, *Journal of Applied Polymer Science,* **89**, 3931-3938(2003).
10. H. Mirzadeh, M. Dadsetan, and N. Sharifi-Sanjani, Platelet Adhesion on Laser-Induced Acrylic Acid-Grafted Polyethylene Terephthalate, *Journal of Applied Polymer Science*, **86**, 3191-3196(2002).
11. B. Gupta, C. Plummer, I. Bisson, P. Frey, and J. Hilborn, Plasma-induced Graft Polymerization of Acrylic Acid onto Poly(ethylene terephthalate) Films: Characterization and Human Smooth Muscle Cell Growth on Grafted Films, *Biomaterials*, **23**, 863-871(2002).
12. Y. C. Nho and O. H. Kwon, Blood Compatibility of AAc, HEMA, and PEGMA-grafted Cellulose Film, *Radiation Physics and Chemistry*, **66**, 299-307(2003).
13. L. M. Ferreiraa, A. N. Falcão, and M. H. Gilb, Elemental and Topographic Characterization of LDPE Based Copolymeric Films Obtained by Gamma Irradiation, *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, **265**, 193-197(2007).
14. M. X. Hua, Q. Yang, and Z. K. Xua, Enhancing the Hydrophilicity of Polypropylene Microporous Membranes by the Grafting of 2-Hydroxyethyl Methacrylate via a Synergistic Effect of Photoinitiators, *Journal of Membrane Science*, **285**, 196-205(2006).
15. B. Rånby, Photochemical Modification of Polymers - Photocrosslinking, Surface Photografting, and Lamination, *Polymer Engineering and Science*, **38**, 1229-1243(1998).
16. R. Schwalm, “UV Coatings: Basics, Recent Developments and New Applications”, Amsterdam, Elsevier, 2007.