ISSN(Print) 1229-0033
ISSN(Online) 2234-036X
http://dx.doi.org/10.5764/TCF.2011.23.3.155

한국염색가공학회지 제23권 제3호 2011년
Textile Coloration and Finishing
Vol. 23, No. 3, 2011

〈Research Paper〉

Reactive Dyeing of Photografted *para*-Aramid Fabrics

Eun Min Kim[1] **and Jinho Jang**[†]

Nano-Bio Textile Engineering, Kumoh National Institute of Technology, Gumi, Korea
[1]SOFOS Co. Ltd., 716 Daechun-dong Dalseo-gu, Daegu, Korea

(Received: August 3, 2011/Revised: September 19, 2011/Accepted: September 21, 2011)

Abstract— *para*-Aramid has limited dyeability because of its highly crystalline structure and compactness. To improve the dyeability of the *para*-aramid to reactive dyes of bright color in deep shade, the fabrics were photografted under continuous UV irradiation with dimethylaminopropyl methacrylamide and 4-benzoyl benzoic acid as a monomer and a hydrogen-abstractable photoinitiator respectively. A UV energy of 35J/cm^2 and a photoinitiator concentration of ten percent or more with respect to the monomer in the formulation was required for optimal photografting. Grafting yield increased with higher monomer application level. Surface analysis indicated significant alterations in the atomic composition of the photografted fabric surface and the fabric surface was covered with the grafted polymers. While the pristine *para*-aramid fabrics showed no appreciable dyeability to the α-bromoacrylamide reactive dyes, the grafted *para*-aramid fabrics enhanced the dyeability to the reactive dyes substantially. In case of C.I. Reactive Blue 50, a K/S value of 8.7 can be obtained with the grafted *para*-aramid fabrics with a grafting yield of 2.3 %. Also the color fastness properties of the dyed fabrics was excellent in the conditions of washing, rubbing and light irradiation.

Keywords: *para-aramid, UV radiation, photografting, surface modification, reactive dyeing*

1. Introduction

Poly (p-phenylene terephthalamide), PPTA, has excellent characteristics of high tensile strength, elastic modulus and inherent flame resistance. *Para*-aramid fibers are widely used in protective apparel, composites, aircraft cargo liners, marine applications and asbestos replacement. However low dyeability of the fibers has limited wider applications in the protective and industrial field$^{1)}$, which may resulted from its highly crystalline structure and compactness$^{2)}$. In the conventional coloration of *para*-aramid fibers, acid-stable pigments should be added into sulfuric acid solution just before spinning head$^{3)}$. To dye the *para*-aramid fabrics using a wet process, the aramid fibers should be swollen for dyes to enter the internal space of fibers without deteriorating the inherent performance characteristics such as mechanical strength and shrinkage, which requires more sophisticated dyeing methods.

Significant studies have been carried out to improve the limited swelling of the aramid fabrics including carrier and solvent dyeing with various swelling agents in the presence of aqueous organic solvent solutions$^{4,5)}$. Also highly thermostable disperse dyes can be used for the high temperature dyeing of the aramid fabrics as high as 190°C$^{6)}$. However, most coloration methods of aramid fabrics caused such inevitable deficiencies as insufficient color build-up and color fastness, decreases in tensile strength, difficult removal of the auxiliaries, long dyeing time and high dyeing temperature, which are not environmentally friendly and energy-saving processes.

Photo-induced grafting or photografting is a very popular technique for the surface modification of polymeric materials, which can be induced by EB, UV irradiation, ionizing radiation, or wet thermal treatments$^{7,8)}$. When textiles are irradiated to UV radiation, the macromolecules creates radicals. which then initiates graft copolymerization reactions of various monomers. Photoinitiator (PI) plays a key role in both photopolymerization and surface photo

---

[†] Corresponding author. Tel.: +82-54-478-7715; Fax.: +82-54-478-7710; e-mail: jh.jang@kumoh.ac.kr

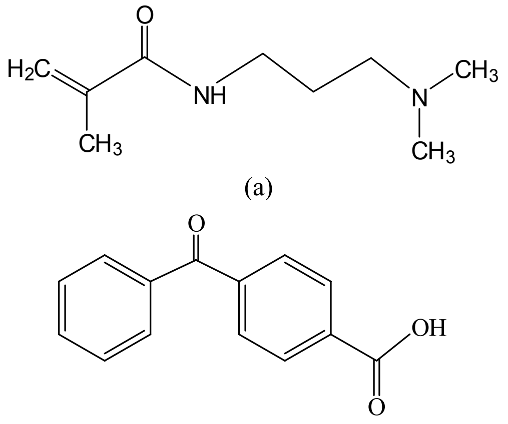
grafting. Standard radical PIs can be classified into cleavable PIs (Norrish type) and the non-cleavable PIs (hydrogen abstraction type). Since the surface photografting depend on the hydrogen abstraction of the polymer surface, the hydrogen-abstractable PIs such as BP have been used for the surface photografting. Benzophenone (BP) and its derivatives are the most commonly used photoinitiators for photografting. However, most of them are water-insoluble and hence the photografting reactions have to be carried out in organic solvents, which induce additional costs and environment problems9). Water-soluble 4-Benzoyl benzoic acid is one of the benzophenone derivatives are commonly used as photosensitizers and photoinitiator in photochemistry, which is known to undergo light-excitation from n to π^* triplet states10,11). Grafting of functional monomers onto synthetic fibers is one of the effective ways to improve or change their dyeability to various dyes.

Many researchers have studied the introduction of functional groups such as carboxylic acid, hydroxyl, or amide onto polymer using various methods12-16). The photografting of PET with vinyl pyrrolidone and acryloyl morpholine as monomers also showed an increased dyeability to reactive dyes and increased affinity to various iodine species which imparted antimicrobial activity17). The photografted PET with a amine-containing monomer showed enhanced dyeability toward the reactive dyes due to the presence of secondary amino groups in the monomer18,19). In this study, the *para*-aramid fabrics were modified with 3-dimethylaminopropyl methacrylamide by UV-induced graft copolymerization using hydrogen-abstractable 4-benzoyl benzoic acid (BBA) as a photoinitiator. The influence of the UV energy, monomer and photoinitiator concentrations on the grafting was investigated. The characterization of the grafted aramid fabrics was carried out by ATR, ESCA and SEM analysis. The dyeability of the grafted aramid fabrics to reactive dyes as well as colorfastness were investigated.

2. Experimental

2.1 Materials and chemicals

para-Aramid fabrics (Kevlar 159, 300denier, 145g/m^2) were supplied by Dupont Co. Ltd. As supplied by Aldrich Chemical Co., N-[3-(Dimethylamino)propyl] methacrylamide and 4-Benzoyl benzoic acid were used as a monomer and a hydrogen-abstractable photoinitiator (PI) respectively. A wetting agent (Triton X100) was bought from Yakuri Pure Chemical Co. Ltd (Kyoto Japan). C.I. Reactive Red 84 and C.I. Reactive Blue 50 were used for dyeing. The chemical structures of the monomer and PI are shown in Scheme 1.



Scheme 1. Molecular structures of (a) monomer and (b) PI.

2.2 Photografting

Aramid fabrics were immersed into the aqueous grafting formulation containing monomer, PI and Triton X100. Then the wetted fabric was squeezed to a wet pick up of about 35% using a padding mangle. A UV irradiator 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 homopolymers. The grafting yield (G%) and grafting efficiency (GE%) which were calculated from the following equations respectively:

$$G\% = \frac{W_3 - W_1}{W_1} \times 100$$

$$GE\% = \frac{W_3 - W_1}{W_2 - W_1} \times 100$$

where, W_1 is the weight of the original fabric, W_2 is the weight of fabric after UV irradiation, 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 which were blended with KBr and made into discs. For the grafted *para*-aramid fabrics, ATR apparatus attached to a ZnSc crystal was used with a Tensor 27 spectrophotometer (Bruker Optics). ESCA (Electron Spectroscopy for Chemical Analysis) was performed on the surface of the grafted aramid fabrics using a X-ray photoelectron spectroscope (K-Alpha, ThermoFisher). The elemental ratios of O_{1s} or N_{1s} to C_{1s} were calculated. A field emission scanning electron microscope (JSM-6500F, JEOL) were used to study the surface morphology of the untreated and grafted aramid fabrics.

2.4 Mechanical and thermal properties

The tensile properties of aramid warp yarns having a linear density of 33.3tex in the fabrics were measured at room temperature using a universal testing machine (Instron 4467) with a crosshead speed of 2 cm/min and the grip length was 10 cm. The specimens were elongated at constant rate and mean values were obtained from testing of ten samples or more. Thermal behavior of the aramid fabrics was observed using a thermogravimetric analyzer (TGA Q500) at a heating rate of 20°C/min to 800°C under nitrogen gas atmosphere. LOI (limiting oxygen index) was measured with an oxygen index combustibility tester (Yasuda Seiki Seisakusho, Japan) according to ISO 4589.

2.5 Reactive dyeing and color fastness

The standard dyeing contained 5%owf dye concentration with 50g/L NaCl at 60°C and pH 7 for 90 min. After the dyeing, the dyed fabrics were washed using a Launder-O-meter (ATLAS, Type LP2) first with 2 wt% detergent solution (ECE Phosphate REF DET B) at 50°C for 30min and subsequently with distilled water at 50°C to remove the unfixed dyes on the fabrics.

A UV/Vis spectrophotometer (Agilent Technologies, US/8453) was used for measuring the dye exhaustion (%E) based on the remaining dyeing liquor at the maximum absorption wavelength before and after the dyeing. K/S was calculated from reflectance at λ_{max} measured with a reflectance spectrophotometer (Gretag Macbeth, Coloreye 3100). The effects of monomer concentration on the dyeability of the grafted aramid fabrics were investigated by the dyeing with the reactive red dyes using an IR dyeing machine (DL-6000, Starlet Co. Ltd.). To investigate the effect of the dye concentration on the dyeability of the grafted aramid fabrics, various concentrations of C.I. Reactive Red 84 and C.I. Reactive Blue 50 were dyed to the grafted *para*-aramid fabrics under the optimum condition. The color fastness tests to laundering, rubbing and light irradiation of the dyed fabrics were carried out with a Launder-O-meter (Daelim Engineering, Korea), Crock meter (Heungshin Engineering, Korea) and Fade-O-meter (Korea Science, Korea) according to KS K ISO 105-C06, KS K 0650 and KS K 0700 respectively.

3. Results and Discussion

3.1 Grafting Yield (G%) and Grafting Efficiency (GE%)

Several factors affecting the photografting treatment of the aramid fabrics were investigated including monomer and PI concentrations as well as UV energy. The 4-benzoyl benzoic acid can abstract hydrogen from *para*-aramid molecules upon UV irradiation and the polymer radicals initiate the graft copolymerization. The monomer is expected to reduce the fast inhibition reaction of atmospheric oxygen due to the presence of two nitrogen atoms in the molecular structure. The optimization of UV energy is very important for the surface photografting, which primarily depend on the initiation efficiency of photoinitiator and the reactivity of monomer[20,21]. Both G% and GE% increased with the increase in UV energy on the grafting such as Fig. 1.

Maximum grafting is obtained when the UV energy is as high as 35J/cm^2 because of the high crystallinity and orientation of the aramid fabrics. It can be understood that larger UV energy may also induce the photodegradation of the grafted chains as well as photopolymerization. The effects of monomer and PI concentrations on the grafting were investigated under UV energy of 35J/cm^2 as given in Table 1.

Higher PI concentration than 10% on the weight of monomer was beneficial in increases in both grafting yield (G%) and grafting efficiency (GE%) on the grafting. The marginal increase in the grafting above the 10% photoinitiator concentration may indicate the enhanced termination of the initiated and propagating radicals by the ketyl radicals of the 4-benzoyl benzoic acid. The grafting yield increased with the increase in monomer concentration because the rate of polymerization is proportional to the monomer content applied on the fabric. However, the grafting efficiency slightly increased with the increase in monomer concentration probably due to the inevitable homopolymerization of the monomer.

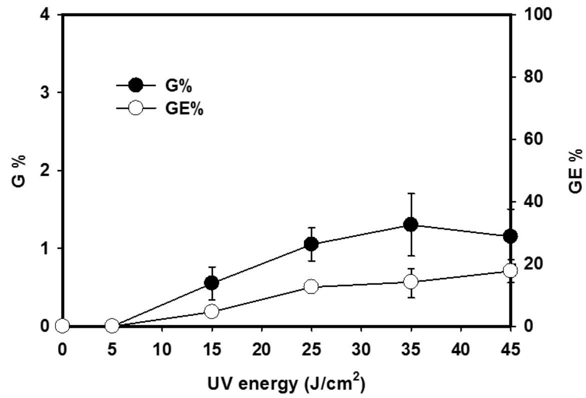


Fig. 1. Effect of the UV energy on the grafting (monomer 40% and PI 10% owm).

Table 1. Effect of the monomer and PI concentrations on the grafting (UV energy 35J/cm^2)

PI (% owm)	Monomer (%)	G%	GE%
0	40	0.0	0.0
5	40	0.0	0.0
10	10	0.0	0.0
	20	0.0	0.0
	30	0.0	0.0
	40	1.3±0.5	13.8±4.9
	60	2.3±0.6	20.4±0.5
	80	4.6±0.3	22.8±0.3
15	40	1.4±0.3	11.7±0.2
20	40	1.2±0.4	8.9±0.3

3.2 Surface analysis

Fig. 2 shows the IR spectrum and ATR spectra of the photopolymerized monomer and the grafted aramid fabrics respectively. Secondary amide carbonyl stretching and N-H bending bands of the photopolymerized monomer located at 1656cm^{-1} and 1537cm^{-1} respectively together with N-H stretching at 3323cm^{-1}. The grafted aramid fabrics showed absorption bands at 3286cm^{-1}, 1635cm^{-1} and 1529cm^{-1} assigned to the stretching vibrations of the amide linkage in the grafted fabric. The subtracted spectrum indicated the presence of the grafted polymer on the surface of aramid fabrics, where the amine and amide vibrations were observed at 3356cm^{-1}, 1660cm^{-1} and 1521cm^{-1}.

Chemical compositions of the grafted aramid fabrics surface were quantitatively characterized by ESCA analysis (Fig. 3, Table 2). Carbon and oxygen content in the outer surface of aramid fabrics decreased significantly with grafting.

The increase in N_{1s} peak at the binding energy

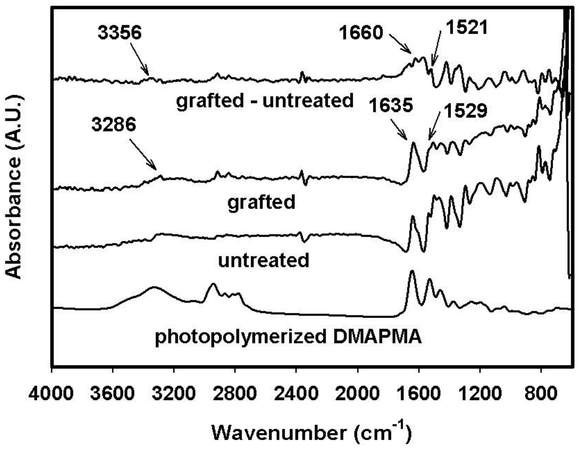


Fig. 2. IR spectra of photopolymerized monomer and ATR spectra of the grafted fabrics.

Table 2. Atomic compositions of untreated and grafted fabrics

Graft (%)	C_{1s} (%)	O_{1s} (%)	N_{1s} (%)	O_{1s}/C_{1s} (%)	N_{1s}/C_{1s} (%)
0.0	78.5	18.4	3.0	23.4	3.8
0.8	75.5	14.9	9.6	19.7	12.7
1.8	74.8	14.5	10.8	19.3	14.4

Table 3. Tensile properties of UV-irradiated, grafted and dyed on aramid yarns

	Untreated	UV-irradiated	Grafted	Dyed
Strength (mN/tex)	851.5±109.4	845.2±121.8	868.6±104.1	861.7±105.3
Modulus (N/tex)	46.5±2.6	43.7±3.1	44.3±3.9	44.5±3.3
Elongation (%)	3.0±0.5	3.2±0.3	3.2±0.6	3.1±0.5

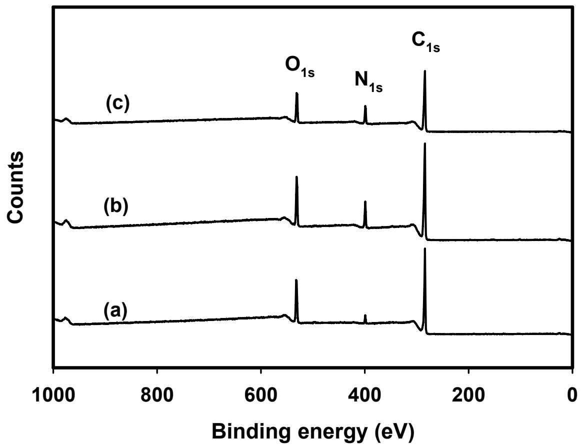


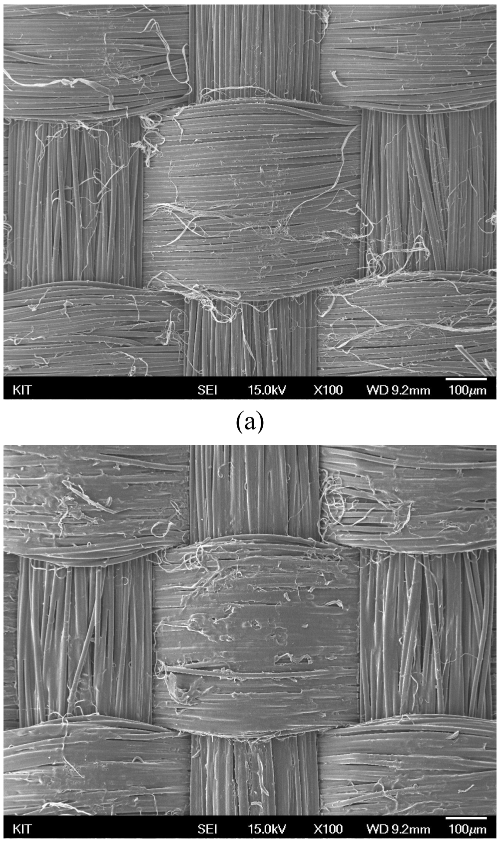
Fig. 3. ESCA spectra of aramid fabrics: (a) untreated, grafted (b) 0.8% and (c) 1.8%.

of 399eV substantiated the presence of nitrogen on the surface of the grafted aramid fabrics. As expected, the atom ratio of N_{1s}/C_{1s} increased with the increase in grafting yield proportionally.

Also the presence of the grafted poly monomer was verified by SEM image as shown in Fig. 4. Compared with the untreated fabrics, the grafted polymer seems to be bound on the aramid fiber surface with some inter-fiber bonds between adjacent fibers, which increased with increasing G%.

3.3 Mechanical and thermal properties

Mechanical properties of the aramid yarns, disintegrated from the aramid fabrics, were tested and summarized in Table 3. The tensile strength, modulus and elongation to break of the aramid yarns were only slightly changed by 2.0%, 4.7% and 4.6% respectively in the case of grafted fabrics compared with those of the untreated fabrics.



(a)

(b)

Fig. 4. SEM images of the aramid fabrics: (a) untreated and (b) 1.8% grafted.

In addition the dyeing process did not deteriorate the mechanical properties as well.

The thermal degradation behavior of the untreated, irradiated, grafted and dyed aramid fabrics were determined by thermo-gravimetric analysis as shown in Table 4.

The maximum decomposition temperature of the untreated *para*-aramid fabrics appeared at 607.7°C

Table 4. TGA analysis and LOI data of UV-irradiated, grafted and dyed aramid fabrics

	DTGA peak (°C)	T_{98} (°C)	T_{75} (°C)	T_{60} (°C)	Char (%)	LOI
Untreated	607.7	528.0	608.2	674.1	54.4	28.9
UV-irradiated	608.7	542.4	609.5	718.2	55.3	28.9
Grafted	609.0	305.8	608.1	674.1	53.9	28.9
Dyed	607.8	312.4	607.3	690.2	54.3	28.9

and those of the grafted and dyed aramid fabrics increased negligibly by 1.3°C and 0.1°C respectively. However the char yield of the grafted and dyed aramid fabrics slightly decreased by 0.5% and 0.1% respectively compared with the untreated fabrics. The effect of the treatment on the flame retardant property was assessed by limiting oxygen index (LOI), which is shown in Table 4. The LOI values of the UV-irradiated, grafted and dyed aramid fabrics did not change noticeably compared with the untreated *para*-aramid fabrics. The surface photografting treatment seemed to have little effect on the bulk properties of the aramid fabrics including mechanical and thermal properties.

3.4 Reactive dyeing

The effect of grafting with monomer concentration condition on the reactive red dyeing was investigated (Fig. 5). It can be seen that both K/S and the exhaustion of the grafted aramid fabrics remarkably increased with increasing monomer concentration.

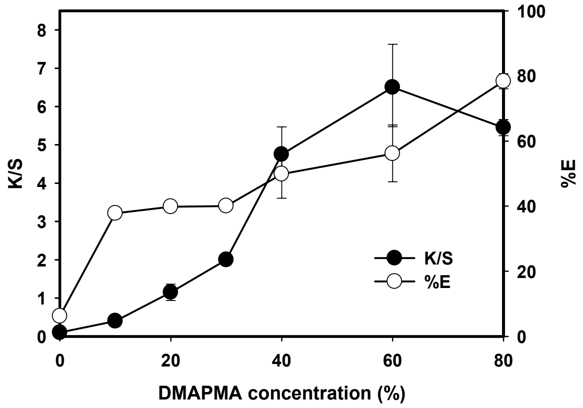


Fig. 5. Effect of monomer concentration on K/S and exhaustion of the grafted aramid fabrics (PI 10%, 35J/cm^2).

While pristine aramid fabrics showed no appreciable dyeability to the reactive red dye, a bright color of deep shade was obtained with the grafted aramid fabrics indicating the covalent bond formation between the secondary amino groups of the grafted monomer and the dyes. Dyeing mechanism may follow the similar reaction mechanism of the α-bromoacrylamido reactive dyes with the amine-containing amino acid residues of wool[22].

The effect of dye concentration on the color build-up properties of the grafted aramid fabrics was shown in Table 5. The grafted fabrics showed higher exhaustion and color yield with increasing dye concentration. The highest K/S of 8.7 was obtained with C.I. Reactive Blue 50, while the C.I. Reactive Red 84 showed lower K/S compared with the blue dye, which may be related with the different affinity and reactive groups of both dyes. However much deeper color shade cannot be obtained even with the highest dye concentration of 7% on the weight of the fabric because the amount of amino groups in the grafted fabrics is limited, which are available to the covalent bond formation of the reactive dyes.

Table 5. Effect of dye concentration on K/S and exhaustion of the grafted aramid fabrics

Dye	Conc.(%)	K/S	%E
Red 84	1	6.2±0.9	94.1±1.1
	2	6.9±1.1	88.3±7.3
	3	7.2±0.3	76.6±0.5
	5	6.6±1.3	56.2±9.0
	7	6.5±0.2	47.1±1.8
Blue 50	1	6.3±0.8	93.7±0.6
	2	7.2±1.1	89.9±2.6
	3	7.8±1.2	81.1±4.4
	5	8.7±0.9	65.8±3.6
	7	8.1±0.2	56.8±2.4

Table 6. The colorfastness of the dyed aramid fabrics

	K/S	Laundering							Rubbing		Light
		Shade	Stain						Dry	Wet	
			Wool	Acrylic	PET	Nylon	Cotton	Acetate			
Red	5.3	3-4	4-5	4-5	4-5	4-5	5	4-5	4-5	4-5	4
	6.7	4	4-5	4-5	5	4-5	4-5	4-5	4-5	4-5	5
Blue	5.5	3-4	4-5	4-5	5	4-5	4-5	4-5	4-5	4-5	3
	7.8	4-5	4-5	5	5	4-5	4-5	4-5	4-5	4-5	4

3.5 Colorfastness

The colorfastness of the dyed aramid fabrics to washing, rubbing and light irradiation was shown in Table 6. The fastness to washing, rubbing and light irradiation is excellent to good. The outstanding color fastness of the grafted *para*-aramid 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 monomer on the fibers. The excellent color fastness can be unique and invaluable advantages considering the very low light colorfastness of *para*-aramid fabrics dyed with cationic dyes and carriers.

4. Conclusions

para-Aramid fabrics were photografted with monomer containing a secondary amino group in order to impart dyeability to reactive dyes. ATR, ESCA and SEM analysis proved that the polymer was grafted on the aramid surface. The K/S value for the grafted fabrics increased remarkably due to the formation of covalent bonds between the secondary amine groups in the grafted polymer and α-bromoacrylamide reactive groups in the dye molecules. The color fastness of the dyed fabric was good including light fastness. The mechanical and thermal properties of aramid fabrics were not deteriorated substantially by the grafting and dyeing treatment compared with other dyeing and modification methods for the aramid fabrics.

Acknowlegement

This work was supported by the Technology Innovation Program (10036532, Hybrid dyeing and finishing technology development of super fibers) funded by the Ministry of Knowledge Economy (MKE, Korea).

References

1. H. H. Yang, “Kevlar Aramid Fiber”, U.S.A., Formerly du Pont Fibers E. I. de Nemours & Co., Inc., pp.12-16, p.111, 1992.
2. J. K. Fink, “High Performance Polymer”, Norwich, William Andrew Inc., pp.423-448, 2008.
3. B. L. Kaul, “Synthetic Fiber Dyeing”, Society of Dyers and Colourists, U. K., pp.230-233, 2004.
4. E. A. Manyukov, S. F. Sadova, N. N. Baeva and V. A. Platonov, Study of Dyeing of Thermostable *para/meta*-Aramid Fibre, *Fibre Chemistry*, **37**(1), 54-58(2005).
5. S. Kobayashi, T. Ito and Y. Sasaki, Dyeing Behavior of Aramid Fibers Treated with Organic Solvents, *Sen-I Gakkaishi*, **51**(1), 34-38(1995).
6. S. Kobayashi, T. Ito and Y. Murase, Dyeing Behavior of Disperse Dyes on Aramid Fibers and the Observation of Their States of Adsorption in the Fiber, *Sen-I Gakkaishi*, **50**(5), 229-236(1994).
7. Q. Wei, “Surface Modification of Textiles”, CRC press Woodhead Publishing Ltd., pp.91-100, 2009.
8. E. M. Kim and J. Jang, The Enhanced Cationic Dyeability of Ultraviolet/ozone-treated *meta*-Aramid Fabrics, *Coloration Technology*, **127**, 173-178(2011).
9. A. Zhao, Z. Li and H. Wang, Acetone/Water as a New Photoinitiating System for Photografting: A Theoretical Study, *Polymer*, **51**, 2099-2105(2010).
10. K. H. Hong and G. Sun, Antimicrobial and

Chemical Detoxifying Functions of Cotton Fabrics Containing Different Benzophenone Derivatives, *Carbohydrate Polymers*, **71**, 598-605(2007).
11. C. Geismann and M. Ulbricht, Photoreactive Functionalization of Poly(ethyleneterephthalate) Track-etched Pore Surface with Smart Polymer Systems, *Macromolecular Chemistry and Physics*, **206**, 268-281(2005).
12. W. Huang and J. Jang, Hydrophilic Modification of PET Fabrics via Continuous Photografting of Acrylic Acid (AA) and Hydroxyethyl Methacrylate (HEMA), *Fibers and Polymers*, **10**(10), 27-33(2009).
13. J. Jang and W. S. Go, Continuous Photografting of HEMA onto Polypropylene Fabrics with Benzophenone Photoinitiator, *Fibers and Polymers*, **9**(4), 375-379(2008).
14. J. Jang and J. A. Son, Cationization of PET Fabrics via Continuous Photografting of [3-(Methacryloylamino)propyl]trimethylammonium Chloride, *Textile Science and Engineering*, **44**(6), 312-318(2007).
15. S. Y. Han and J. Y. Jaung, Acid Dyeing Properties of Meta-aramid Fiber Pretreated wity PEO45-MeDMA Derived from [2-(Methacryloyloxy)ethyl] Trimethylammonium Chloride, *Fibers and Polymers*, **10**(4), 461-465(2009).
16. J. Jang and J. A. Son, Improved Thermal Stability of PET Fabrics by Photografting of Methacryloxypropyltrimethoxysilane(MAPTMS), *Textile Coloration and Finishing(J. Korean Soc. Dyers & Finishers)*, **20**(4), 1-7(2008).
17. W. Huang and J. Jang, Photografting of PET Fabrics with Vinyl Pyrrolidone and Acryloyl Morpholine Monomers, *Textile Coloration and Finishing*, **20**(5), 28-34(2008).
18. W. Huang and J. Jang, Reactive-dyeable Treatment of PET Fabrics via Photografting of Dimethylaminopropyl Methacrylamide, *Textile Coloration and Finishing*, **21**(2), 40-47(2009).
19. Y. Dong, W. S. Lyoo and J. Jang, Union Dyeing of the Photografted PET/Wool Blend Fabrics with Dimethylaminopropyl Methacrylamide, *Fibers and Polymers*, **11**(2), 213-217(2010).
20. K. Studer, C. Decker, E. Beck, and R. Schwalm, Overcoming Oxygen Inhibition in UV-curing of Acrylate Coatings by Carbon Dioxide Inerting: Part I, *Progress in Organic Coating*, **48**, 92-100(2003).
21. K. Studer, C. Decker, E. Beck, and R. Schwalm, Overcoming Oxygen Inhibition in UV-curing of Acrylate Coatings by Carbon Dioxide Inerting: Part II, *Progress in Organic Coating*, **48**, 101-111(2003).
22. D. M. Lewis, “Wool Dyeing”, Bradford, Society of Dyers and Colourists, pp.225-226, 1992.