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Reactive Dyeing of Meta-aramid Fabrics Photografted with Dimethylaminopropyl Methacrylamide

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Abstract: Aramid fibers have been known to difficult to dye with conventional dyes and dyeing techniques because of its extremely high crystallinity and compactness. In order to make the aramid fibers dyeable to a bright color in deep shade, *meta*-aramid fabrics were photografted under continuous UV irradiation with dimethylaminopropyl methacrylamide (DMAPMA) and benzophenone as a monomer and a hydrogen-abstractable photoinitiator respectively. Several factors affecting the photografting treatment of the meta-aramid fabrics were investigated including monomer and photoinitiator concentrations. ATR, ESCA and SEM analysis indicated significant alterations on the chemical structure and atomic composition of the photografted fabric surface and the fabric surface was covered with the grafted polymers. While the pristine meta-aramid fabrics showed no appreciable dyeability to the α-bromoacrylamide type reactive dyes, the grafted aramid fabrics showed the remarkably enhanced dyeability to the reactive dyes, which was proportional to the graft yield indicating the covalent bond formation between the dyes and the secondary amino groups in the grafted DMAPMA. In case of C.I. Reactive Red 84, a *K/S* value of 14.8 can be obtained with the grafted meta-aramid fabrics with a graft yield of 7.6 % (w/w). Also and the color fastness properties of the dyed fabrics was excellent in the conditions of washing, rubbing and solar irradiation.

Keywords: Meta-aramid, Photografting, UV irradiation, Reactive dyes, Dyeability

Introduction

Meta-aramid is a high performance polymer having resistance to wide range of organic solvent, high melting point, and excellent flame resistance with low levels of smoke generation [1]. Because of their nonflammable aromatic structures of high C/H ratios, meta-aramid fabrics have been exploited for the applications requiring both high thermal resistance and flame retardency [2].

The aramid fiber is difficult to be colored to deep shade with conventional dyeing techniques because of its extremely high glass transition temperature and high crystallinity. Therefore cationic dyes are exclusively used in the exhaust dyeing of meta aramid fibers with the help of special dyeing auxiliaries such as carriers. And for the coloration of para aramid fibers pigments should be added into sulfuric acid solution just before spinning head [3].

In order to dye the aramid fabrics, 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 supercritical fluid dyeing [4,5], liquid ammonia pretreatment [6], carrier and solvent dyeing with various swelling agents in the presence of aqueous solvent solutions containing dimethyl formamide, dimethyl sulfoxide and so forth [7-10]. Also highly thermostable disperse dyes can be used for the high temperature dyeing of the aramid fabrics as high as 190 °C [11]. 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.

The reactive dyes is one of the environmentally friendly dyes for wool fibers because of the absence of metals and it has an excellent colorfastness property with a bright shade. The reactivity of the wool reactive dyes having α-bromoacrylamide group can form a covalent bond with nucleophilic moieties in wool such as SH, NH_2 and OH groups. The reaction of these dyes proceed via either nucleophilic substitution of the bromine atom or 1,2-Michael addition across the double bond of the α-bromoacylamido groups with certain amino residues of wool protein. Regardless of the pathway involved, the intermediates can cyclise to form an aziridine ring and crosslink wool protein [12].

Grafting functional monomers onto synthetic fibers is one of the effective ways to improve or change the dyeability to various dyes. 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, hydroxyl, or amide onto polymer using various methods [13-17]. 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

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*Corresponding author: jh.jang@kumoh.ac.kr friendliness, and low energy consumption as explained in previous study [18].

In previous study, meta-aramid films surface was modified by UV/O_3 irradiation, and the dyeability of aramid films to cationic dyes increased due to higher hydrophilic its of the irradiated films surface and strong electrostatic attraction between the cationic dyes and anionic dyeing sites of the meta aramid [19]. 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 activity [20]. The photografted PET with DMAPMA showed enhanced dyeability toward the ractive dyes due to the presence of secondary amino groups in DMAPMA. The optimized photografting and dyeing conditions of DMAPMA onto PET and PET/wool were previously reported [21,22].

The characterization of the grafted meta-aramid fabrics with DMAPMA was carried out by ATR, ESCA and SEM analysis. The dyeing behavior of the grafted meta-aramid fabrics to reactive dyes was investigated, including the effect of grafting and dyeing condition. Furthermore, the grafting and reactive dyeing for meta-aramid fabrics may overcome the loss in the mechanical and thermal properties associated with the conventionally recommended dyeing methods for the meta-aramid fabrics.

Experimental

Materials and Chemicals

Meta-aramid fabrics (Nomex, 60^s, 55 g/m^2) were supplied by Dupont Co. Ltd. and were used for the study. As supplied by Aldrich Chemical Co., N-[3-(Dimethylamino)propyl] methacrylamide (DMAPMA) and Benzophenone (BP) were used as a monomer and a hydrogen-abstractable photoinitiator (PI) respectively. Ethanol was used to dissolve BP in the DMAPMA. A wetting agent (Triton X100) was bought from Yakuri Pure Chemical Co. Ltd. (Kyoto Japan). C.I. Reactive Red 84, C.I. Reactive Blue 50 and C.I. Reactive Yellow 39 were used for dyeing. The chemical structures of monomer, BP and reactive dyes are shown in Figure 1 and Figure 2.

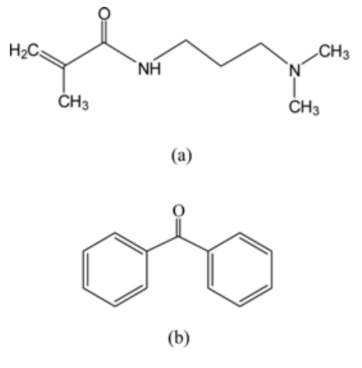


Figure 1. Molecular structures of (a) DMAPMA and (b) BP.

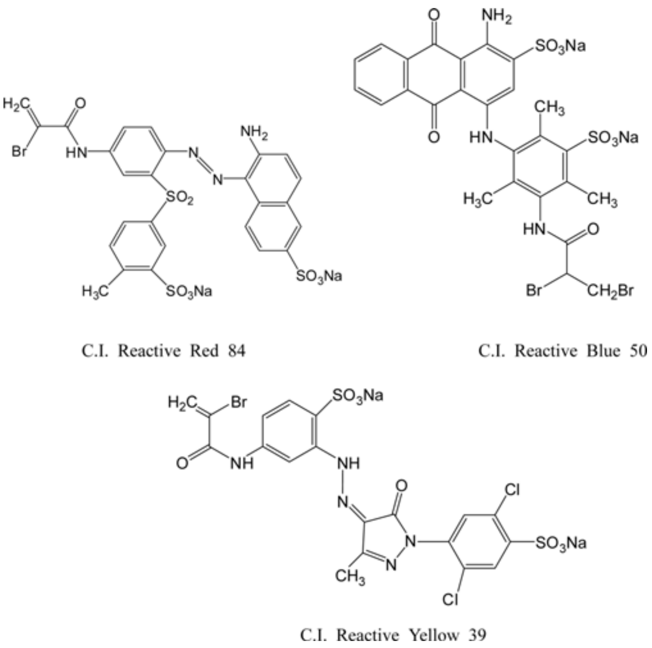


Figure 2. Molecular structures of reactive dyes.

Photografting and Dyeability

Meta-aramid fabrics were immersed into the grafting formulation containing monomer, PI and Triton X100. Then the wetted fabric was squeezed to a wet pick up of about 90 % using a padding mangle. A UV apparatus enclosing a D-bulb (a metal doped mercury lamp) of 80 W/cm intensity was used for UV irradiation. D-bulb was chosen to maximize the photografting corresponding to the maximum absorption wavelength of BP [14]. 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.

The effects of UV energy, PI and monomer concentration were investigated by dyeing of the grafted meta-aramid fabrics with the reactive blue dyes. The dyeing was carried out using an IR dyeing machine (DL-6000, Starlet Co. Ltd.). The standard dyeing conditions were 5 %owf dye concentration with 50 g/*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 30 min 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 exhaustion (%E) based on the remaining dyeing liquor at the maximum absorption wavelength before and after dyeing. *K/S* was calculated from reflectance at $\lambda_{\max}$ measured with a reflectance spectrophotometer (Gretag Macbeth, Coloreye 3100).

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 meta-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 meta-aramid fabrics using a X-ray photoelectron spectroscope (K-Alpha, ThermoFisher). The elemental ratio of O_{1s} or N_{1s} to C_{1s} was calculated. A field emission scanning electron microscope (JSM-6500F, JEOL) were used to study the surface morphology of the untreated and grafted meta-aramid fabrics.

Mechanical and Thermal Properties

The tensile properties of warp meta-aramid yarns having a linear density of 9.8 tex 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 meta-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 ISO4589.

Reactive Dyeing and Color Fastness

To investigate the effect of the dye concentration on the dyeability of DMAPMA-grafted meta-aramid fabrics, various concentrations of C.I. Reactive Red 84, C.I. Reactive Blue 50 and C.I. Reactive Yellow 39 were applied to the grafted meta-aramid fabrics in 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.

Results and Discussion

Grafting of DMAPMA and Dyeability to Reactive Dye

Photografting can be controlled by changing photopolymerization condition such as UV absorption, concentration of monomer and photoinitiator, as well as irradiation condition such as spectral intensity of an irradiator, UV energy and atmosphere inertness. Present continuous system tends to facilitate oxygen inhibition of the initiating polymer radicals due to high conveyer speed and absence of inert nitrogen gas [23]. The benzophenone can abstract hydrogen from meta-aramid molecules upon UV irradiation and the polymer radicals initiate the graft copolymerization. The DMAPMA 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 [24,25]. Both G% and GE% increased with the increase in UV energy on the DMAPMA grafting. Maximum grafting is obtained when the UV energy is as low as 15 J/cm^2 because of the high dyeability of the grafted copolymer on meta-aramid fabrics. The effects of DMAPMA and BP concentration on the grafted meta-aramid fabrics were investigated under a UV energy of 15 J/cm^2 as given in Table 1. Grafting yield (G%) increased with the increase in monomer concentration because the rate of polymerization is proportional to the monomer content applied on the fabric. However, grafting efficiency (GE%) slightly decreased with the increase in monomer concentration probably due to the inevitable homopolymerization of the monomer. A higher BP concentration was beneficial in increases in both G% and GE% on the on the DMAPMA grafting. The marginal increase in the grafting with the larger photoinitiator concentration may indicate the enhanced termination of the initiated and propagating radicals by the ketyl radicals of the benzophenone.

The effect of grafting with DMAPMA and BP concentration condition on the reactive blue dyeing was investigated as

Table 1. Effect of DMAPMA and BP concentration on the grafted meta-aramid fabrics

BP (% owm)	DMAPMA (% owb)	5	10	20	30	40	50
10	G%	0.0	0.4±0.1	1.8±0.1	6.8±0.3	7.6±0.5	10.5±1.1
	GE%	0.0	15.7±0.2	19.9±3.5	31.3±0.9	25.7±1.4	29.7±0.8
20	G%	0.0	0.7±0.2	2.7±0.2	7.0±0.2	8.6±0.5	11.8±0.3
	GE%	0.0	14.6±1.6	21.5±2.9	32.0±1.1	29.9±0.8	31.4±0.2

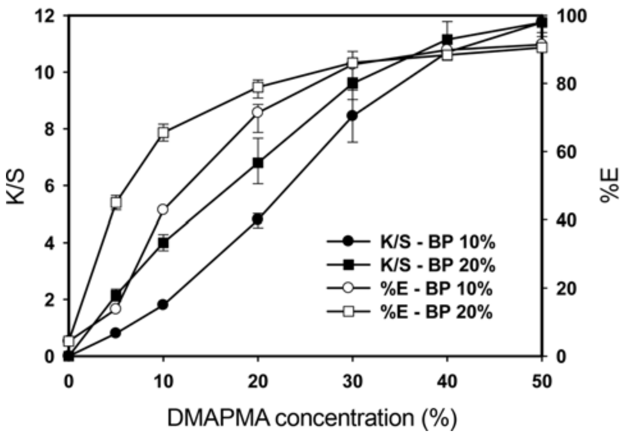


Figure 3. Effect of the DMAPMA and BP concentration on *K/S* and exhaustion of the grafted meta-aramid fabrics (15 J/cm^2).

shown in Figure 3. It can be seen that both *K/S* and the exhaustion of the grafted meta-aramid fabrics remarkably increased with increasing DMAPMA and BP concentration condition. While pristine meta-aramid fabrics showed no appreciable dyeability to the reactive blue dye, a bright color and deep shade was obtained with the grafted meta-aramid fabrics indicating the covalent bond formation between the secondary amino groups of the grafted DMAPMA and the dyes. Dyeing mechanism may follow the similar reaction mechanism of the α-bromoacrylamido reactive dyes with the amine-containing amino acid residues in wool [13].

Surface Analysis

Figure 4 shows the IR spectrum and ATR spectra of the photopolymerized DMAPMA the grafted meta-aramid fabrics respectively. The photopolymerized DMAPMA showed the N-H stretching at 3340 cm^{-1} and the secondary amide carbonyl stretching and N-H bending bands of the poly DMAPMA appeared at 1643 and 1531 cm^{-1} respectively. Also the grafted meta-aramid fabrics showed absorption bands at 3261, 1643, and 1523 cm^{-1} assigned to the stretching vibrations of the amide linkage in the grafted fabric. The subtracted spectrum indicated the presence of the grafted DMAPMA on the surface of meta-aramid fabrics, where the amine and amide vibrations were observed at 3375, 1627, and 1550 cm^{-1}.

Chemical compositions of the grafted meta-aramid fabrics surface were quantitatively characterized by ESCA analysis (Figure 5, Table 2). Carbon content in the outer surface of meta-aramid fabrics did not change significantly with grafting, while oxygen content decreased. The increase in N$_{1s}$ peak at the binding energy of 399 eV substantiated the presence of nitrogen on the surface of the grafted meta-aramid fabrics. The atom ratio of N$_{1s}$/C$_{1s}$ increased with the increase in grafting yield proportionally. Also the presence of the grafted poly (DMAPMA) was verified by SEM image as shown in Figure 6. Compared with the untreated fabrics, the grafted poly (DMAPMA) seems to be bound on the

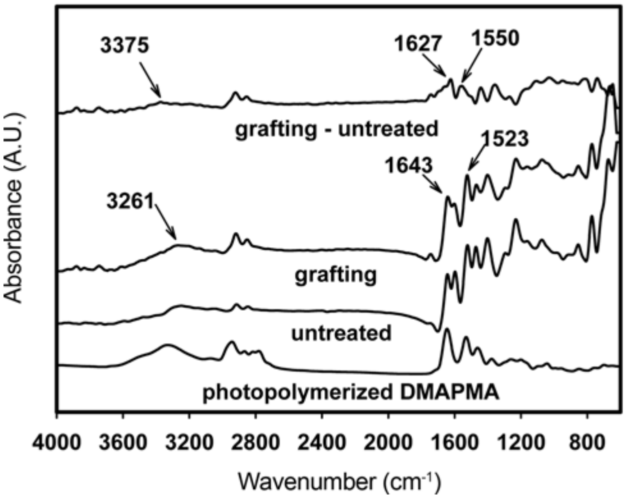


Figure 4. IR spectrum of photopolymerized DMAPMA and ATR spectra of the grafted meta-aramid fabrics.

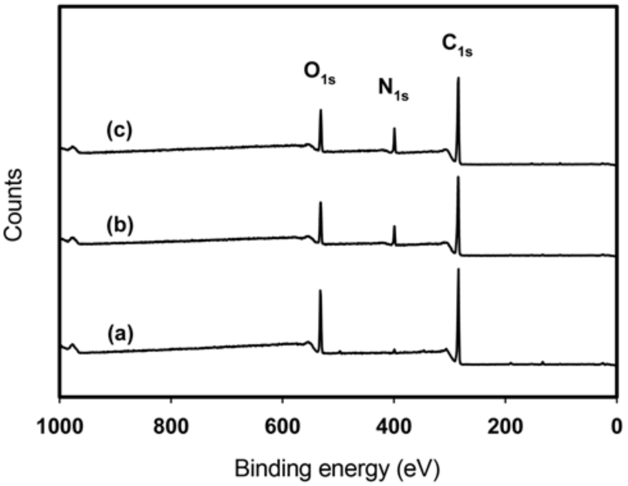


Figure 5. ESCA spectra of the meta-aramid fabrics; (a) untreated, grafted, (b) 1.5 %, and (c) 10.5 %.

Table 2. Atomic compositions of untreated and grafted meta-aramid fabrics

Grafting (%)	C$_{1s}$ (%)	O$_{1s}$ (%)	N$_{1s}$ (%)	O$_{1s}$/C$_{1s}$ (%)	N$_{1s}$/C$_{1s}$ (%)
Untreated	76.3	21.8	1.9	28.6	2.5
1.5	75.5	16.1	8.4	21.3	11.2
10.5	76.3	13.7	10.0	17.9	13.1

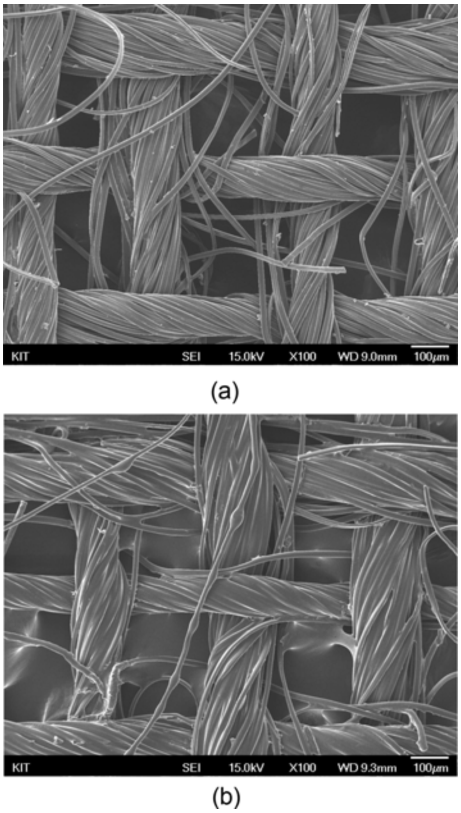


Figure 6. SEM images of the meta-aramid fabrics; (a) untreated and (b) grafted (8.1 %).

meta-aramid fiber surface with some inter-fiber bonds between adjacent fibers, which increased with increasing G%.

Mechanical and Thermal Properties

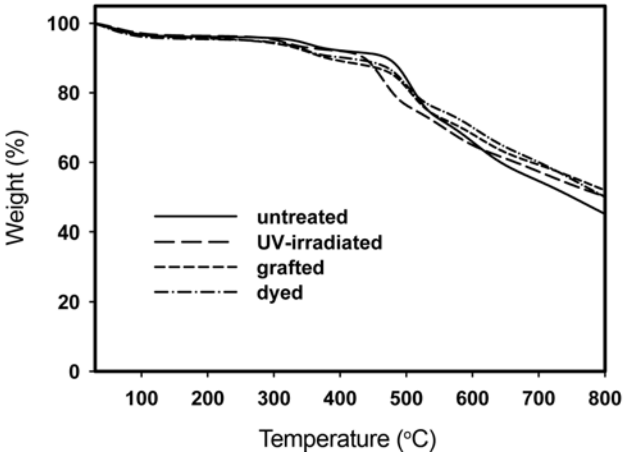


Figure 7. TGA thermodiagrams of the meta-aramid fabrics.

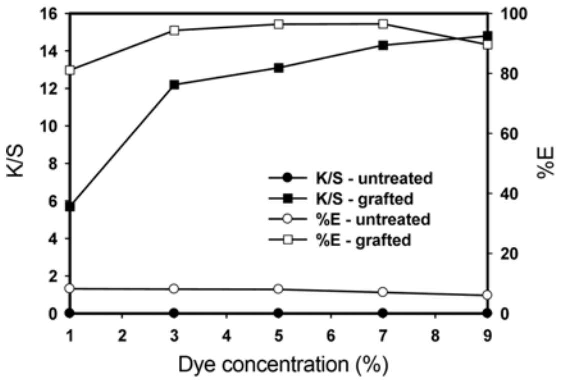
Mechanical properties of the meta-aramid yarns, disintegrated from the aramid fabrics, were tested as shown in Table 3. While the tensile strength of the meta-aramid yarn slightly decreased by 2.1 % in the grafted and subsequently dyed fabrics, the modulus and elongation to break significantly decreased by 12 and 18 % respectively. However the extent of decreases by the grafting treatment for the higher dyeability was far less than those by the other dyeing and modification methods [6,8,9]. The thermal degradation behavior of the untreated, irradiated, grafted and dyed aramid fabrics determined by thermo-gravimetric analysis was shown in Figure 7 and Table 4. The maximum decomposition temperature of the untreated meta-aramid fabrics appeared at 506.8 °C, while those of the grafted and dyed meta-aramid fabrics decreased marginally by 0.4 and 8.1 °C respectively. However the char yield of the grafted and dyed aramid fabrics significantly increased by 6.8 and 4.9 % respectively compared with the untreated meta-aramid 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 meta-aramid fabrics did not change noticeably compared with the untreated meta-aramid fabrics. The surface photografting treatment seemed to have little effect on the bulk properties of the aramid fabrics such

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

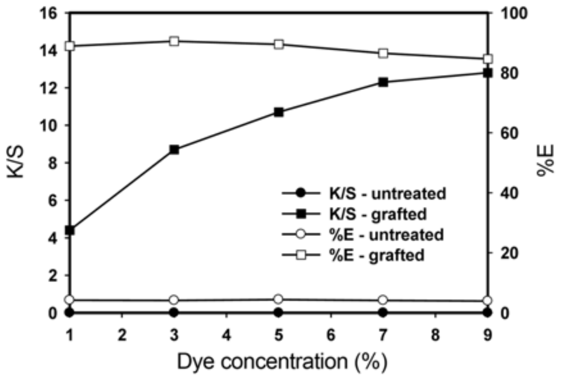
	Untreated	UV-irradiated	Grafted	Dyed
Strength (mN/tex)	195.2±34	192.2±43 (-1.5 %)	191.4±27 (-2.0 %)	191.1±38 (-2.1 %)
Modulus (mN/tex)	2,962±373	3,042±423 (+2.7 %)	2,704±634 (-8.7 %)	2,605±444 (-12.0 %)
Elongation (%)	28.7±6	26.2±8 (-8.7 %)	24.9±6 (-13.3 %)	23.6±9 (-17.7 %)

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

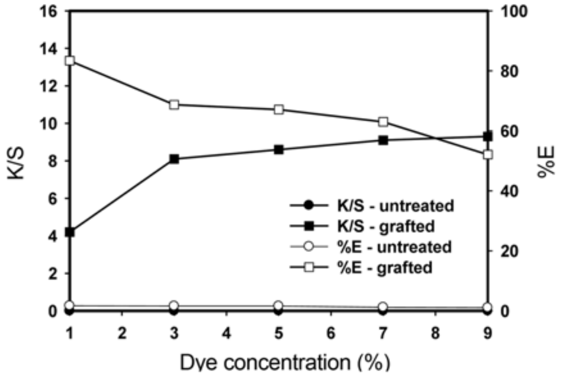
	DTGA peak (°C)	T_{95} (°C)	T_{75} (°C)	T_{55} (°C)	Char (%)	LOI
Untreated	506.8	332.4	532.5	695.3	45.1	27.2
UV-irradiated	465.1	307.2	512.9	730.1	50.2	27.2
Grafted	506.4	266.5	531.9	759.7	51.9	27.2
Dyed	498.3	271.1	551.4	751.1	50.0	27.2



(a) C.I. Reactive Red 84



(b) C.I. Reacitve Blue 50



(c) C.I. Reactive Yellow 39

Figure 8. Effect of dye concentration on *K/S* and exhaustion of the meta-aramid fabrics.

as mechanical and thermal properties.

Reactive Dyeing

The effect of dye concentration on the color build-up properties of the DMAPMA-grafted meta-aramid fabrics was shown in Figure 8. While the untreated meta-aramid fabrics apparently had no dyeability to the reactive dyes with very low exhaustion, the grafted fabrics showed higher exhaustion and color yield with increasing dye concentration. The highest *K/S* of 14.8 was obtained with C.I. Reactive Red 84, while the C.I. Reactive Yellow 39 and C.I. Reactive Blue 50 showed lower *K/S* compared with the red dye, which maybe related with the difference in affinity and the chemical structures of the reactive groups of the three dyes. However much deeper color shade cannot be obtained even with the highest dye concentration of 9 % 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.

Color Fastness

The color fastness of the dyed fabrics to washing, rubbing and light were shown in Table 5. The fastness to washing, rubbing and light is excellent to good. The outstanding color fastness of the grafted meta-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 DMAPMA on the fibers. The excellent color fastness can be unique and invaluable advantages considering the very low light colorfastness of meta-aramid fabrics dyed with cationic dyes and carriers.

Conclusion

Meta-aramid fabrics were photografted with DMAPMA containing a secondary amino group in order to impart dyeability to reactive dyes. ATR, ESCA and SEM analysis proved that the DMAPMA polymer was grafted on the surface of meta-aramid. 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.

Table 5. The colorfastness of the dyed meta-aramid fabrics to laundering, rubbing and light irradiation

Reactive dyes	*K/S*	Laundering							Rubbing		Light
		Shade	Stain						Dry	Wet	
			Wool	Acrylic	PET	Nylon	Cotton	Acetate			
Red 84	12.2	4-5	4-5	4-5	4-5	4-5	4-5	4-5	5	4-5	5
	14.3	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	5
Blue 50	8.7	4-5	4-5	4-5	5	4-5	4-5	5	4-5	5	4
	12.3	4-5	4-5	4-5	4-5	4-5	4-5	5	4-5	5	4
Yellow 39	8.1	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	5
	9.1	4-5	4-5	4-5	4-5	4-5	4-5	4-5	5	4-5	5

The color fastness of the dyed fabric was excellent including light fastness. The mechanical and thermal properties of meta-aramid fabrics were not deteriorated substantially by the grafting and dyeing treatment compared with other dyeing and modification methods for the meta aramid fabrics.

Acknowlegement

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