

Controllable Surface Modifications of Polyamide by Photo-Induced Graft Polymerization Using Immobilized Photo-Initiators

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Received 19 October 2009; accepted 4 December 2009

DOI 10.1002/app.31909

Published online 22 February 2010 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A novel two-step UV initiated grafting method has been developed and applied on surface modification of polyamide. Anthraquinone-2-sulfonate sodium, an acid dye, was chosen as the photo-initiator. In the first step, photo-initiators were ionically bonded onto polyamide through a normal acid dye dyeing process. Vinyl monomers such as acrylic acid were then grafted onto polyamide surface in the following step. During UVA irradiation, not only monomers were grafted onto polymer surface, photo-initiator itself was also covalently bonded onto polymer. The grafted polymers were characterized by

Fourier transform infrared spectrometer (FTIR), X-ray photoelectron spectroscopy (XPS) and scanning electron microscope (SEM). The degree of photo-grafting can be controlled by adjusting concentrations of photo-initiator and monomer, as well as UVA exposure time. This process demonstrated the feasibility of efficiently modifying polymer surface under low UV intensity. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 3629–3637, 2010

Key words: photo-initiator; acid dyes; UV; grafting; polyamide; acrylic acid

INTRODUCTION

Polymers are applied everywhere in our daily life due to their excellent mechanical and processing properties. However, in many applications, commodity polymer surfaces should be chemically modified to obtain desirable functions such as biocompatibility, proper adhesion, antistatic ability, antifouling ability, super hydrophobicity etc., without altering their original good mechanical, thermal, physical or chemical properties.^{1–3} Among the available surface modification technologies, surface grafting is a rather useful technology and has advantages in grafting chains onto polymer surface without changing bulk properties; long-term durability due to strong covalent bonds between graft chains and polymer surfaces.^{1,2}

The grafting methods can be generally divided into two categories, i.e., “grafting-from” (graft polymerization monomers from surface) and “grafting-to” (direct coupling existing polymer molecules to the surface) processes.^{2,4,5} Although it would be ideal to use grafting-to process to precisely control

grafted chain structures on surfaces of fibers, there are specific requirement for reactive groups on surface.² On the other side, there are more choices to implement the grafting-from process, including graft polymerizations by direct chemical modification,^{6,7} initiated with plasma or ultraviolet (UV) irradiation.^{1,8,9} UV induced radical grafting process can easily modify surface structures of polymeric fibers without changing their bulk properties and has been widely applied to modify polymer surface since 1950s.^{8–11}

When photo-initiators are excited and formed the triplet state, they can abstract hydrogen from either polymer or monomers. Therefore, high homopolymerization rate of monomers is a great concern in UV initiated radical graft polymerization on surfaces of materials.^{8–15} And if the photo-initiators are immobilized onto the polymers, there will be more chances for them to abstract hydrogen from polymer surface. New immobilization methods have been proposed to overcome this issue in recent years. For example, Ma et al. proposed the sequential method: initiators were first fixed on the surface by coupling benzopinacol upon UV irradiation. However, high energy was needed to break the covalent bond between benzopinacol and polymer surface in the second step.¹⁰ There is also synergist immobilization photo-polymerization method,¹¹ which used tertiary amine to immobilize benzophenone onto polymers, while tertiary amine can also enhance the photo-

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Contract grant sponsor: National Science Foundation; contract grant number: CTS 0424716.

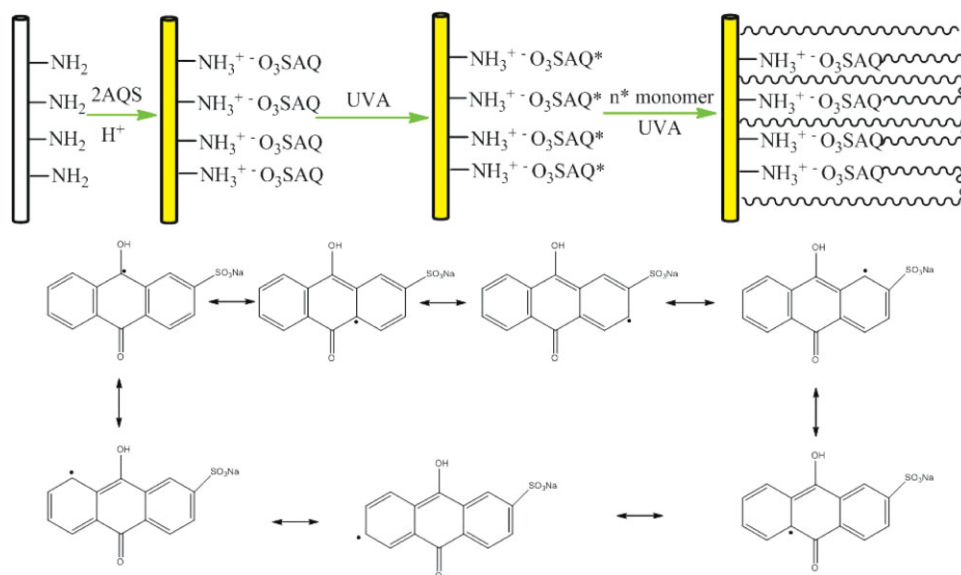


Figure 1 Schematic diagram of 2AQS radical resonance structures of one ketone site after photo-excitation and hydrogen abstraction. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

grafting reaction. In this study, we developed an easier way to immobilize photo-initiators onto polymer surface by dyeing polyamide fibers with anthraquinone-2-sulfonate sodium. Anthraquinone-2-sulfonate sodium (2AQS) is both a “good photo-sensitizer”¹² and an acid dye, thus, it can form ionic bonds with polyamide surfaces under acidic condition, i.e. acid dyeing. Then the dyed polymers can be used to directly graft monomers under UV irradiation. Compared with commonly used photoinitiator benzophenone, 2AQS is water soluble and high grafting rate has been obtained even though the UV lamp is only less than 100W, while the normal lamp used for UV grafting is a couple of thousands watt. All these features decide this method is an economic, eco-friendly and efficient way to modify polymer surface.

EXPERIMENTAL

Materials

Polyamide 6, 6 filament taffeta (306A), was purchased from Testpolymers (West Pittston, PA). Acrylic acid, anthraquinone-2-sulfonate sodium was purchased from Aldrich. All other chemicals were supplied by major chemical vendors and used as received. UV irradiation was conducted in Spectrolinker XL-1500 UV crosslinker (Spectroline), with six 15w lamps in 365 nm wavelength, the distance between UV tube and material is 14 cm. All water used in this study was deionized water.

Immobilization of photo-initiators

A dyeing process was used to immobilize photo-initiators onto polyamide and was conducted on a lab-

oratory scale dyeing machine (Atlas, USA). Dyeing bath temperature was raised to 49° by a heating rate of 5°C/min from room temperature, and then was increased to 95° by a rate of 0.5°C/min and kept at 95° for 60 min. The rotation speed was 35rd/min and the dye concentration was ranging from 0.5 to 2.5% (owf). Sodium sulfate was used as an auxiliary in a concentration that was five times of the dye concentration. Dyeing bath pH was adjusted to three by using sulfuric acid. Then, dyed fabric was washed in hot water for 30 min to remove unbonded dyes.

Graft polymerization

The dyed fabric was dipped into a solution with monomer concentrations ranging from 2 to 30%, and then was padded in a wringer machine. Wet pick-up rate was controlled between 50 and 70%. The padded fabric was exposed to UVA irradiation for different time duration. Finally, the finished fabric was Soxhleted in water for 24 hrs to remove any ungrafted reagents. Figure 1 gives out a schematic diagram of the whole reaction process.

Dye extraction test

This test was conducted on dyed and then grafted sample and dyed only samples, respectively, by immersing in a sodium hydroxide (pH = 12) solution (0.01 M) and shaking for 30 min at 90°C. Because photo-initiators were immobilized onto polyamide through ionic bond in the dyeing process, addition of sodium hydroxide can break these ionic bonds and remove all the photo-initiators from the

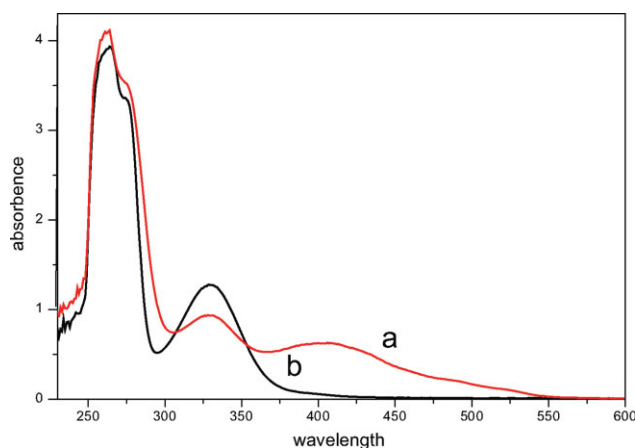


Figure 2 UV-vis absorbance spectra of 2AQS aqueous solutions before (b) and after (a) UVA irradiation. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

polyamide fibers. However, if there are new bonds formed during the photo-grafting reaction between photo-initiators and polyamide, photo-initiators could survive the test and stay on the polymers.

The degree of grafting was evaluated by comparing the weight difference before and after grafting on dyed polymers.

$$\text{Grafting rate} = \frac{W_{\text{aftergrafting}} - W_{\text{beforegrafting}}}{W_{\text{beforegrafting}}} \times 100\%$$

Before weighing, polymers were dried in a vacuum oven at 45° for 12 hrs.

Characterizations

Fourier transform infrared (FTIR) spectroscopy was performed with a Nicolet 6700 FTIR spectrometer (Thermo Scientific) with a resolution of 4 cm⁻¹. A field emission scanning electron microscope (FE-SEM) (Philips XL30) was used for high-magnification observation. UV-vis absorption spectra were taken with an Evolution 600 UV-visible spectrophotometer (Thermo Scientific) in a wavelength range of 200–600 nm with a 1-cm quartz cell. XPS was per-

formed on PHI 5600 Multi-Technique system (Perkin-Elmer, Schwerzenbach, Switzerland). Mg-Kalpha radiation (non-monochromatized) was used, and operated at 300 W. Color coordinates were measured according to CIELAB color scale relative to the standard daylight source D65 and fluorescent lamp F2 on a reflection spectrophotometer (Color-Eye 7000A, GretagMacbeth Instruments) over undyed polyamide sample. Fluorescent microscope Leica DM 2500 (Leica Microsystems, Germany) was used to observe photo-initiators immobilized onto the polymer.

RESULTS AND DISCUSSION

Immobilization of photo-initiators

An anthraquinone dye, anthraquinone-2-sulfonate sodium (2AQS) was immobilized on polyamide fibers by using an acid dyeing process. The 2AQS dyed polyamide fibers became light yellow after dyeing since the dye has a weak absorbance in UV-Vis range [Fig. 2(b)]. The light yellow color became brownish after UVA (365nm) exposure, which is consistent with the color change of the dye solution^{16–20}(Fig. 2). In addition, a colorimeter (Color Eye 7000A) was applied to quantitatively evaluate color changes. Each measurement was expressed in the CIE *L*a*b** system. *L** stands for lightness and varied from 0 (black) to 100 (white); *a** represents red (positive) and green (negative); and *b** is positive for yellow color and negative for blue color. Thus, compared with CIE *L*a*b** values of a standard sample, negative ΔL^* means darker, more red gives positive Δa^* , and positive Δb^* is more yellow. Dyed polyamide (trial 1), UVA-exposed dyed polyamide (trial 2), and grafted polyamide (trial 3) samples were measured against untreated polyamide. The results (Table I) show that under all the light sources, trial 1 sample became darker, greener, and yellower than the standard. The same trend was observed for trial 2 sample, except it was darker, yellower, and redder than trial 1 sample. Compared with trial 2, trial 3 the grafted sample was redder, but trial 2 UV exposed dyed sample was yellower. The color

TABLE I
Color Coordinates of Undyed, Dyed, and Grafted Samples

	Light source	<i>L*</i>	<i>a*</i>	<i>b*</i>	ΔL	Δa	Δb
Undyed polyamide (standard)	D65	74.701	-0.772	-3.413	n/a	n/a	n/a
	CWF_2	74.493	-0.473	-3.971	n/a	n/a	n/a
Dyed polyamide (trial 1)	D65	74.389	-2.44	2.963	-0.312	-1.668	6.377
	CWF_2	74.387	-1.664	3.482	-0.105	-1.191	7.453
UV-exposed dyed polyamide (trial 2)	D65	72.563	-1.488	7.115	-2.442	-0.666	10.397
	CWF_2	72.828	-1.039	8.359	-1.972	-0.531	12.192
Grafted polyamide (trial 3)	D65	72.022	-1.216	6.598	-2.679	-0.444	10.011
	CWF_2	72.268	-0.755	7.832	-2.225	-0.282	11.803

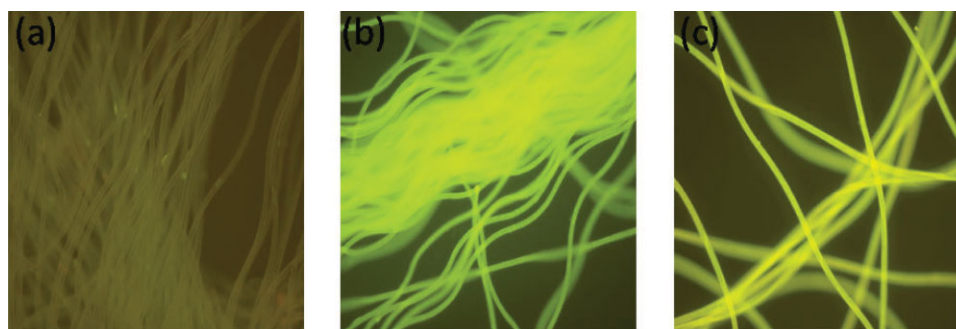


Figure 3 Fluorescent images of undyed polyamide (a), dyed polyamide (b), and photo-grafted polyamide with acrylic acid (c). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

change between undyed sample and dyed sample is due to the incorporation of dyes onto polyamide; the color change between dyed and UV exposed dyed sample is consistent with the solution color change before and after UV exposure, which probably caused by the structural changes of photo-initiator upon UV irradiation^{16,20} and the difference between UV exposed dyed sample and grafted sample may be caused by the interaction between acrylic acid, water and photo-initiator during UV irradiation and photo-grafting polymerization. Fluorescent images of undyed polyamide, dyed polyamide and photo-grafted polyamide are shown in Figure 3. After dyeing, the sample shows very strong fluorescent effect. The grafted sample still shows fluorescent effect, just with lower intensity. The lost part of fluorescent in-

tensity was caused by photo-initiation process. The existence of color on dyed, dyed and photo-grafted polyamide as well as the fluorescent effect indicated successful incorporation and retention of the dye on the polymer.

FTIR results

Chemical structures of all polyamide fabric samples were further confirmed by using FTIR. Compared with untreated polyamide [Fig. 4(a)], the original amide I (1650.8 cm^{-1}) and amide II (1540.2 cm^{-1}) peaks slightly shifted to 1643.1 cm^{-1} and 1532.0 cm^{-1} , respectively for dyed polymer, and the peak intensity at 1532.0 cm^{-1} also increased, which is caused by the ketone groups of photo-initiators;

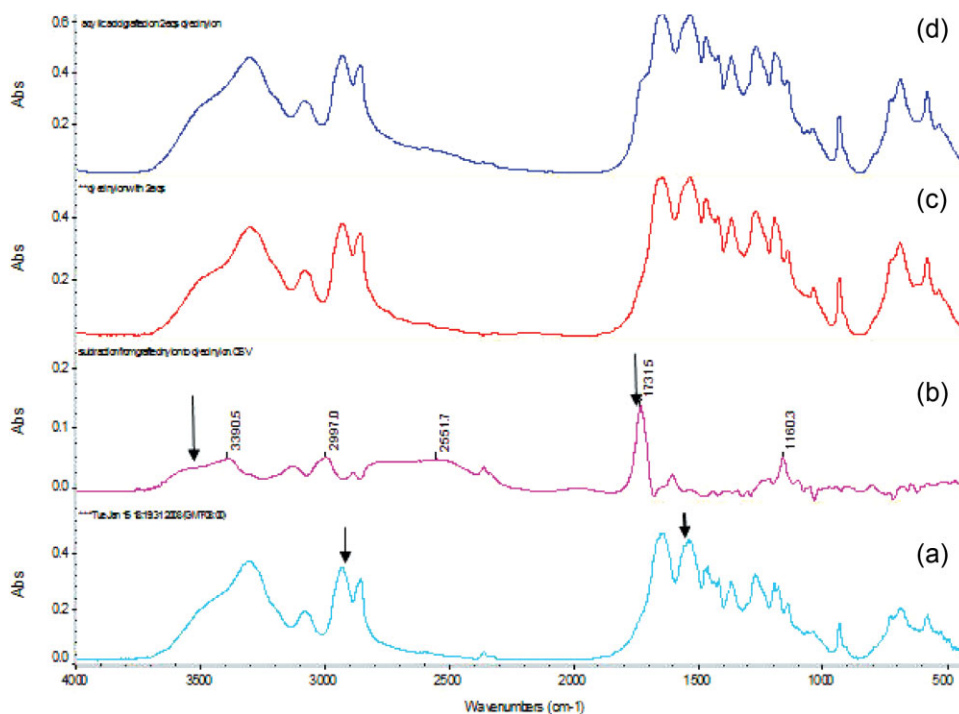


Figure 4 FTIR spectra of original polyamide (a), subtracted spectrum of dyed polyamide from 6% polyacrylic acid grafted polyamide (b), dyed polyamide (c), and polyacrylic acid grafted polyamide (d). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE II
Elemental Contents, O/C and N/C Ratio Before and After UV Exposure

	O content (%)	C content (%)	N content (%)	O/C ratio (%)	N/C ratio (%)
Dyed polyamide	12.51	81.15	6.34	15.4	7.81
Grafted polyamide (3.48% grafting rate)	15.54	80.72	3.75	19.3	4.65
Grafted polyamide (8.23% grafting rate)	28.29	71.12	0.59	39.8	0.83

Increased intensity at 2929.7 cm^{-1} and 2858.9 cm^{-1} was due to the characteristic peaks of benzene ring of photo-initiators. Compared with FTIR spectrum of the dyed only polyamide [Fig. 4(c)], a new shoulder at 1731 cm^{-1} , which is the characteristic peak of carboxylic acid group, could be observed from the dyed and then photo-grafted polyamide sample [Fig. 4(d)]. A subtracted FTIR spectrum [Fig. 4(b)] of the dyed sample from the grafted sample shows more characteristic bands of polyacrylic acid. Besides the peak at 1731 cm^{-1} (C=O from the COOH), the peaks at 2990 cm^{-1} (new C—H bond from CH₂) and the peak at 1160 cm^{-1} (OC—OH) are the bands of grafted acrylic acid.²¹ Under UV irradiation, the excited photo-initiator should first form radicals, which can then abstract hydrogen from N—H bond of amide group because of the relative low energy of N—H bond. The characteristic peaks of tertiary amide at 1607 cm^{-1} (C=O stretch) proved the reaction.^{22,23} The new small peak at 3127 cm^{-1} can be assigned to C—H (from monomer) connected to aromatic ring.²⁴ The characteristic peak of hydroxyl group at 3381 cm^{-1} also could be a result of hydroxyl groups formed from ketone groups in the photo-initiator during the photoreaction process.

XPS study

X-ray photoelectron spectroscopy (XPS) was applied to measure elemental content and bonding energy changes on the surfaces of two samples, dyed and then grafted with 3.48 and 8.23% monomer, respectively. Table II summarizes elemental content changes before and after the grafting reaction. Because acrylic acid has highest oxygen content compared to both polyamide and the photo-initiator, increase of oxygen contents on surfaces grafted fibers was expected. As shown in Table II, the oxygen contents of the polyamide samples grafted with 3.48 and 8.23% monomer concentrations increased from 12.51 to 15.54 and 28.29%, respectively. The nitrogen contents of the two grafted polyamide samples dramatically decreased from 6.34% to 3.75% and 0.59%, respectively, consistent to the expected increase of oxygen content caused by the increased grafting of acrylic acid on the fiber surfaces.

Because XPS can give signals based on specific bonding energy, deconvolution was applied to analyze possible oxygen bonds in the polymer and their intensities. Figure 5 gives XPS of the dyed only polyamide sample, and three peaks can be deconvoluted to oxygen in C=O (532.5 eV) of the amide group, oxygen in hydrogen bonded C=O (531.3 eV) of the amide group, and oxygen in carbonyl group (531.5 eV) from the dyes. Table III summarizes the specific positions, areas and full width at half maximum of the peaks. For the two grafted samples, a new peak at 532.2 eV was formed, which could be assigned to —OH on the newly formed dye structure during UV

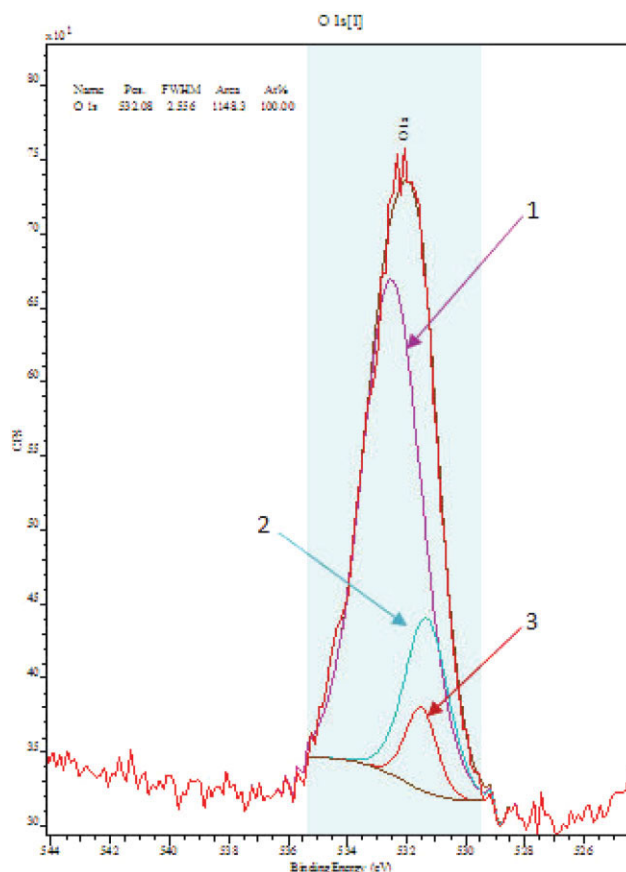


Figure 5 XPS spectrum of dyed polyamide. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE III
Summary of Three XPS Spectra

Sample	Dissolved peak	Chemical bond	Name	Position	Area	FWHM	Concentration
Dyed sample	1	C=O (Amide)	O 1s	532.5	859.4	2.367	8.67
	2	Hydrogenated C=O (Amide)	O 1s	531.3	220	1.721	2.22
	3	C=O (Dyes)	O 1s	531.5	74.5	1.23	0.75
Grafted sample with 3.48% grafting rate	1	C=O (Amide)	O 1s	532.5	860.7	1.909	10.25
	2	Hydrogenated C=O (Amide)	O 1s	531.3	339.6	1.755	4.05
	3	C=O (Dyes)	O 1s	531.5	32.6	0.838	0.39
	4	—OH (dye)	O 1s	532.2	113.3	1.084	1.35
	5	C=O (OH)	O 1s	533.6	2.1	0.918	0.03
	6	(C=O)—OH	O 1s	533.1	3.9	0.425	0.05
Grafted sample with 8.23% Grafting rate	1	C=O (Amide)	O 1s	532.5	1519.9	1.407	21.81
	2	Hydrogenated C=O (Amide)	O 1s	531.3	200	1.787	2.87
	3	C=O (Dyes)	O 1s	531.5	50	1.000	0.72
	4	—OH (dye)	O 1s	532.2	45.2	0.800	0.65
	5	C=O (OH)	O 1s	533.6	113	1.104	1.62
	6	(C=O)—OH	O 1s	533.1	33.5	0.8	0.48

irradiation, another new peak at 533.6 eV can be assigned to C=O on the monomer acrylic acid, and the third new peak at 533.1 eV can be assigned to the —OH of acrylic acid. The results indicate that when monomer concentration was increased, carboxylic acid groups on surfaces of the grafted samples increased accordingly. While the grafted acrylic acid creates hydrophilic surfaces on the fibers, the grafted polyamide should be able to absorb more moisture and exhibit increased hydrophilicity on the surfaces of the materials. Overall XPS results further confirmed successful photo-grafting of acrylic acid on the dyed polyamide fibers.

SEM results

Surface morphology of the grafted and ungrafted polyamide samples was examined by using scanning electron microscopy (SEM). Figure 6 shows the SEMs of the original fabric (a), the dyed only fabric (b), and the dyed and grafted with 4.16% (c), and 8.23% monomer (d) concentrations, respectively. Both the original and dyed only samples showed smooth surfaces, while the two grafted samples demonstrated rougher surfaces, possibly caused by unevenly grafted acrylic acid. The diameter of grafted samples seems increased a little as well. When monomer concentration was raised, more monomers could be grafted onto polyamide. But at the same time, more acrylic acid also causes rougher fiber surfaces, as observed in Figure 6.

Controllability

Reaction efficiency of the UVA induced radical graft polymerization was investigated by varying photo-

initiator concentration, UV exposure time, and monomer concentration on the surfaces, with results shown in Figures 7–9 respectively. The degree of grafting of acrylic acid on polyamide versus different dye concentrations was conducted by dyeing polyamide with different concentrations of 2AQS, and then immersing samples in 6% (w/v) of monomer. The samples were exposed to UVA irradiation for 2 h. Figure 7 shows that the degree of grafting of acrylic acid increased accordingly as the photo-initiators concentration (owf) was raised from 0.5 to 2.5% in the dyeing bath, and then the degree of grafting on the fibers becomes saturated when the dye concentration was above 1.5%. Acid dyeing on polyamide follows the Langmuir adsorption isotherm, an ionic interaction between the protonated amino groups of the fibers and the dye. Since only limited protonated amino groups exist in the polyamide, increase in dye concentration in the dyeing bath will reach a saturation of the dyes on the surface, which consequently affected grafted monomers on the surfaces.

Increase of UV exposure time has influence on the degree of grafting, which is shown in Figure 8. Polyamide fabric samples dyed with 1.5% of 2AQS (owf) were dipped in 6% acrylic acid solution and then were exposed under UVA irradiation for 0.5, 1, 2, 3 and 8 hrs, respectively. The degree of grafting increased greatly initially, but after 2 hrs, the increase rate became very low. Theoretically, if there is enough monomer, increase the UVA exposure time will increase grafting rate. However, when grafting reaction happens, acrylic acid also evaporates at the same time due to an elevated temperature caused by UVA irradiation. Therefore, after 2 hrs, there was not much acrylic acid left on the

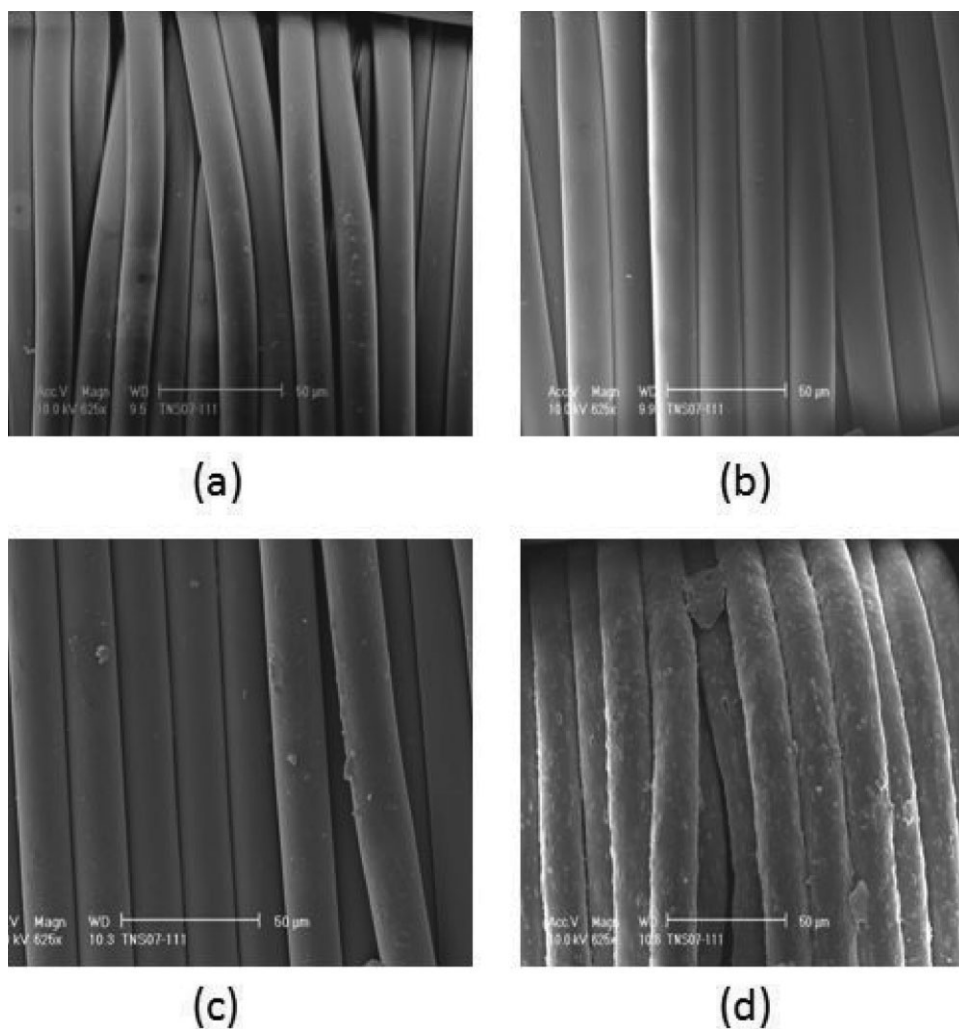


Figure 6 SEM pictures of original polyamide (a), dyed polyamide (b), grafted polyamide (4.16% grafting rate) (c) grafted polyamide (8.23% grafting rate) (d).

sample surface. Thus, a combination of different factors of the reaction resulted in a flattened degree of grafting after 2 hrs exposure (Fig. 7).

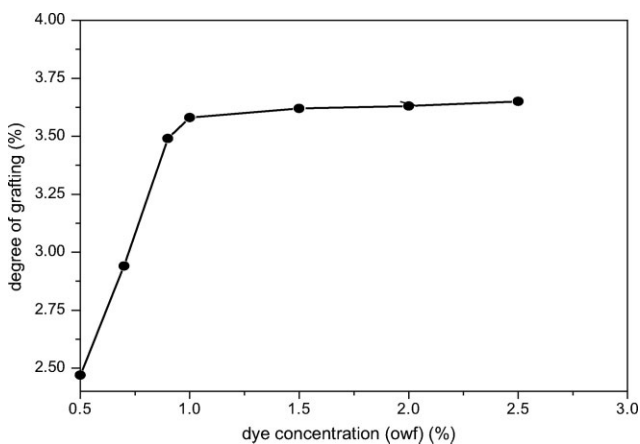


Figure 7 Degree of grafting versus different 2AQS concentration (0.5 wt % AQS, 0.9 wt % AQS, 1.0 wt % AQS, 1.5 wt % AQS, 2.0 wt % AQS, 2.0 wt % AQS), UVA exposure time 2hrs, acrylic acid concentration 6% (w/v).

The relationship between the monomer concentration and degree of grafting is shown in Figure 9. Samples dyed with 1.5% 2AQS (owf) were dipped

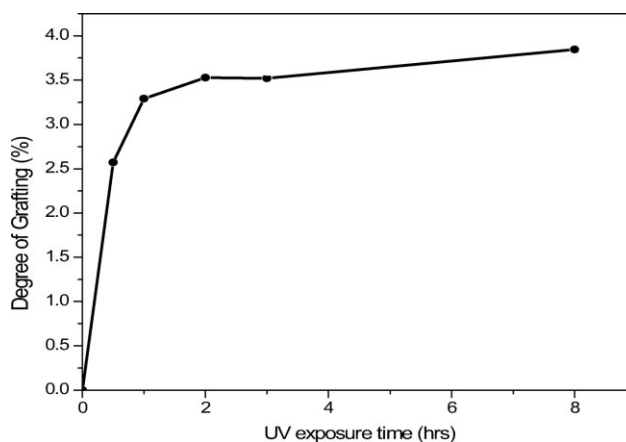


Figure 8 Degree of grafting versus UVA exposure time (0.5, 1, 2, 3, and 8 hr), AQS concentration 1.5 wt %, acrylic acid 6% (w/v).

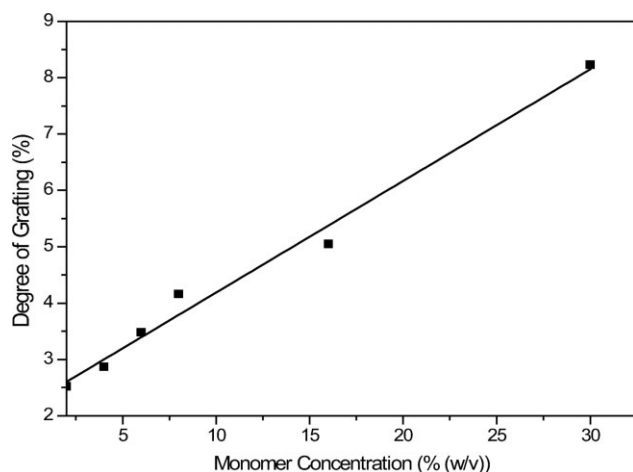


Figure 9 Degree of grafting versus acrylic acid concentration [2% (w/v), 4% (w/v), 6% (w/v), 8% (w/v), 16% (w/v), 30% (w/v)], UV exposure time 2 hrs, 2AQS concentration 1.5 wt %.

into monomer solutions with concentrations varied from 2 to 30%. It shows that the degree of grafting increased when the concentration of the monomer increases. This result suggests the formation of longer side chains with high concentration of monomers in finishing baths.

Potential photo-grafting reactions

Photo-induced reactions of anthraquinone compounds have been studied exclusively.^{13–19} However, using anthraquinone structures such as 2AQS as photo-initiators for radical graft polymerization on polyamide fibers has not been reported, particularly under UVA irradiation. The grafting of acrylic acid on polyamide was confirmed by FTIR, XPS results. From the dye extraction test, we found the color of dyed only samples completely lost, and the extraction solution became reddish, which may be caused by the interactions between dyes and sodium hydroxide. However, the grafted samples showed no apparent color change before and after the test. Sodium hydroxide can break the ionic bonding between photo-initiators and polyamide and therefore dissolve photo-initiators in the solution, but obviously was unable to break the interactions between the dye and polyamide after photo-grafting reaction, an indication of structural changes in the material after the photo-reaction. UV-vis spectra of dye extraction solutions of dyed polyamide sample and photo-grafted sample are given in Figure 10. The extraction solution of the dyed polyamide sample gives a strong absorption peak in the range of 300 to 375 nm, which is very similar to 2AQS UV-vis spectrum. Very weak absorbance is observed from the extraction solution of the grafted sample in this

range. It can be explained that most of the bonding between photo-initiators and polymers are no longer ionic bonds any more. During the grafting process, more than 90% of photo-initiators were covalently bonded onto polyamide polymer based on the UV-vis spectra. As a Norrish Type II photo-initiator, 2AQS can be excited from its ground state to singlet state upon UVA exposure. And the singlet can transfer to a triplet state quickly. The triplet anthraquinone will abstract hydrogen from nearby polyamide substrate, possibly weak N–H bond in the amide group. The photo-initiator radicals could either couple with polymer macro-radicals directly or react with monomer to have a grafting reaction on the initiator. Meantime, the formed polyamide radical can also initiate the addition reaction of monomers. Figure 1 shows the whole process of this novel photo-grafting method and 2AQS radical resonance structure. During the photoreaction process, if there is only one carbonyl group activated, there will be seven resonance structures. If both carbonyl groups are activated, there will form more than 20 resonance structures. Due to the complexity of these photo-initiator radical resonance structures, specific bonding between monomer, polymer substrate and 2AQS, as well as 2AQS and polyamide is still not very clear, but the extraction test results proved that after the photo-grafting process, photo-initiators were also connected onto polymers by covalent bonds.

CONCLUSIONS

A novel photo-initiated grafting method by using acid dye Anthraquinone-2-sulfonate sodium as photo-initiator was developed to modify polymer surfaces. These anthraquinone dyes were immobilized onto polyamide fibers through a facile dyeing process. The incorporated dyes exhibited photo-induced activity upon UVA irradiation. With

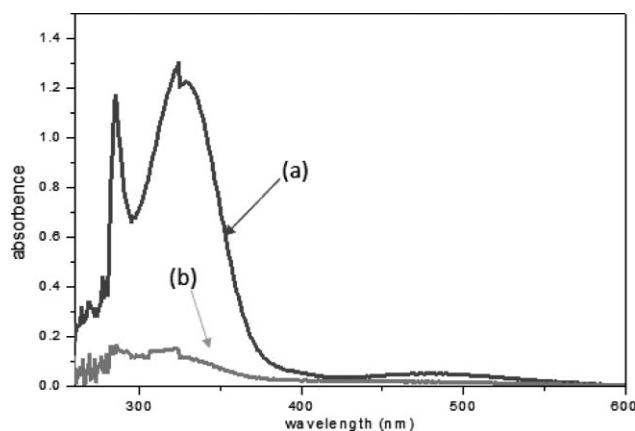


Figure 10 UV-vis absorbance spectra of extraction solutions of 2AQS dyed sample (a) and 2AQS dyed and photo-grafted sample (b).

existence of acrylic acid, a graft polymerization of the monomer on surfaces of the polyamide fibers occurred. FTIR, XPS, SEM, fluorescent and color index data proved the successful grafting of the monomers on the fibers. In addition, the degree of grafting of the monomers could be controlled by varying the monomer concentration, photo-initiator concentration and UVA exposure time. Although the specific bonding between photo-initiators, polymerized monomer and polymer substrate is not clear yet, the extraction tests showed that after the photo-grafting process, photo-initiators were also connected onto polymers by covalent bonds. Compared with existing UV initiated photo-grafting methods, the whole process is not only much easier but also very efficient. The grafting was conducted under 90 Watt UVA lamps; therefore it is also an energy-saving method and has potential applications in modifying any materials containing amine group with different vinyl monomers to obtain desirable surface.

N. Liu is grateful to Jastr Graduate Student Research Fellowship Award at University of California, Davis.

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