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Light-induced surface graft polymerizations initiated by an anthraquinone dye on cotton fibers

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ABSTRACT

Anthraquinone and its derivatives could serve as photo-sensitizers and generate radicals and reactive oxygen species in polymers under exposure of UVA or day light. Such a property was utilized in development of novel light-induced surface radical graft polymerizations on cotton fibers that were dyed with an anthraquinone derivative, 2-ethylanthraquinone. Several functional monomers were directly grafted onto the dyed cotton fibers upon UVA exposure. The chemical and morphological structures and thermal properties of the grafted fibers were confirmed and characterized by Fourier transform infrared spectrometer (FTIR), scanning electron microscope (SEM) and thermal gravimetric analysis (TGA). Reaction conditions including concentrations of the photosensitizer, the amount of monomers, as well as UVA irradiation time could influence grafting efficiencies. More interestingly, the surface graft polymerization did not significantly change the light active functions of the agent, evidenced by the light-active antimicrobial functions of the grafted fibers.

1. Introduction

As the demands on functional polymers and textiles increasing elsewhere, various chemical modification technologies have been developed on fibers and fabrics. Surface modifications and functionalizations of fibrous materials are especially attractive and widely employed to prepare textiles with functions such as hydrophilicity, hydrophobicity, anti-fouling, antimicrobial, improved dyeability, adhesion, and even biocompatibility (Goddard & Horchkiss, 2007; Liu, Chen, Wu, Shen, & Lin, 2010; Uyama, Kato, & Ikada, 1998; Yang, Xu, Dai, Wang, & Ulbricht, 2005; Yu, Kang, Liu, & Mi, 2014; Yu & Urban, 2009; Zhu, Bahramian, Gibson, Schreuder, & Sun, 2012). Radical graft polymerizations initiated by different methodologies have advantages in high controllability, large selectivity range of functional monomers, and durability of resulted functions on the fibers (Berlin & Kislenko, 1992; Cupta, Anjum, Jain, Revagade, & Singh, 2004; Deng, Wang, Liu, & Yang, 2009; Xu, Wang, Shen, Men, & Xu, 2002). Different radical initiation technologies such as atomic transfer radical polymerization (ATRP), glow discharge, γ-ray, corona discharge, remote plasma, and UV irradiation make the radical graft polymerization applicable on almost all polymer surfaces (Bhattacharya & Misra, 2004; Edmondson, Osborne, & Huck, 2004; Furtado & Gomes, 2006; Goddard & Horchkiss, 2007; Lopergolo, Catalani, Machado, Rela, & Lugao, 2000; Suzuki, Kishida, Iwata, & Ikada, 1986; Uyama et al., 1998; Wavhal & Fisher, 1992).

Among those methods, light-induced radical polymerization is an excellent option for surface modifications of fibers and fabrics because of its simplicity, safety, and the low energy in comparison to others (Uyama et al., 1998; Xu et al., 2002; Yagci, Jockusch, & Turro, 2010). During the reaction, a photo-sensitizer is excited to its singlet state that can undergo intersystem crossing to its triplet state under UV light. And the triplet compound can then abstract labile hydrogen from the substrate polymer to form polymer and initiator radicals, which can lead to subsequent radical polymerizations. The polymer radical can result in graft polymerization after reacting with monomers, while the initiator radical may form undesired homopolymerization of monomers, which could lower the grafting efficiency. In addition, if the excited triplet photo-sensitizer abstracts hydrogen from a monomer instead from the polymer, it will not result in graft polymerization on the polymers. Therefore, it is necessary to select polymers possessing very labile hydrogen and monomers without any labile hydrogen. Different approaches have been used to maximize the graft polymerizations on polymers. For example, Bowman et al. developed a highly efficient two-step process in which semipinacol radicals of benzophenone were first coupled to material surfaces, and then followed by photo-initiated polymerization in the presence of monomers (Ma, Davis, & Bowman, 2000). Hong, Liu, and Sun (2009) immobilized a photo-sensitizer onto polymers through chemical

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reactions to minimize the homopolymerization of monomers in solutions. Although those methods successfully improved the grafting efficiency, the treatment processes were less practical due to the additional reactions to incorporate photo-sensitizers onto polymers.

Some anthraquinone compounds are highly light-active (Allen, Pullen, Shah, & Edge, 1995; Shah, Allen, Edge, Navaratnam, & Catalina, 1996) and are able to serve as Norrish type II photosensitizers (Corrales, Catalina, Peinado, & Allen, 2003; Fouassier, Savary, Lalevee, Allonas, & Ley, 2010; Liu & Sun, 2011; Pullen et al., 1996). Anthraquinone compounds are the second abundant class of colorants based on chemical structures. Many light-active anthraquinone compounds possess structural features of vat dyes, which could be easily incorporated onto cellulosic fibers through a conventional vat dyeing process. Thus coloration and immobilization of photosensitizers onto cotton fabrics can be achieved simultaneously in one wet treatment, a potentially economical and environmentally friendly process. The cellulose could serve as a good hydrogen donor in the Norrish type II reaction, generating active sites to initiate radical graft polymerizations.

As a concept proof study, a highly light-active compound, 2-ethylanthraquinone (2EtAQ) (Green, 2010; Zhuo & Sun, 2013), though not a real vat dye due to the low substantivity to cotton fabrics, was incorporated onto cotton fabrics through the vat dyeing process. Monomer solutions were padded onto the 2EtAQ dyed fabrics and then the fabrics were exposed to UV light for initiation of the surface radical graft polymerizations. Two hydrophilic monomers (acrylamide (AAm) and [2-(methacryloyloxy) ethyl] dimethyl-(3-sulfopropyl) ammonium hydroxide (DMMSA)) and three hydrophobic monomers (butyl acrylate (BA), 1*H*, 1*H*, 5*H*-octafluoropentyl acrylate (OFA), and styrene (STY)) were chosen in the trials to evaluate the selectivity and feasibility of the 2EtAQ initiator system. In addition, the 2EtAQ treated cotton fabrics have demonstrated light-induced antibacterial functions (Zhuo & Sun, 2013). The effect of the grafted polymers on the original light-induced antimicrobial activities were evaluated against Gram-negative (*Escherichia coli*) and Gram-positive (*Staphylococcus aureus*) bacteria strains. Chemical and morphological structures of the surface grafted cellulose materials were examined by using FTIR and SEM.

2. Experimental and methods

2.1. Materials

Bleached and desized cotton fabrics (no. 400) were purchased from Testfabric, Inc. (West Pittston, PA). Sodium dithionite and 2-ethylanthraquinone (2EtAQ) were purchased from ACROS Organics (Pittsburgh, PA). Acrylamide (AAm) was purchase from EMD Chemicals (Gibbstown, NJ), [2-(methacryloyloxy) ethyl] dimethyl-(3-sulfopropyl) ammonium hydroxide (DMMSA), styrene (STY), and butyl acrylate (BA) were purchased from Aldrich Co. (MO, USA). 1*H*,1*H*,5*H*-octafluoropentyl acrylate (OFA) was obtained from TCI (TCI America). Inhibitor removers were used to eliminate inhibitors in monomers. All other reagents were supplied by Fisher Scientific (Pittsburgh, PA), and used as received.

2.2. Immobilization of photo-sensitizers

A conventional vat dyeing process was conducted to incorporate the photosensitizer, 2-ethylanthraquinone (2EtAQ), onto cellulose fabrics with concentrations varied from 1% to 9% owf (on weight of fabric). A designated amount of 2EtAQ was dispersed evenly in alkali aqueous solution (pH > 11), and sodium dithionate (molar ratio of photosensitizer:sodium dithionate = 1:20) was added to react with 2EtAQ at 50 °C for 10 min, reducing the chemical to its leuco salt structure that is substantive to cellulose (Zhuo & Sun, 2013). Cotton fabrics were immersed into the prepared dye bath, and kept for 50 min with continuous agitation at room temperature. Sodium sulfate was added as an electrolyte in a ratio of five times more than that of 2EtAQ to improve exhaustion of the chemical onto cellulose. The exhaustion stage was followed by oxidation of the leuco-form of the compound in the fabrics back to the original insoluble anthraquinone structure in the air at room temperature. All treated samples were then thoroughly washed in boiling detergent solution for 30 min, rinsed and dried at conditioned environment overnight.

2.3. Light-induced graft polymerization

The light-induced surface modifications of cotton fabrics were conducted in a UV crosslinker (Spectrolinker XL-1000, Spectroline, USA), with five 8 W UVA lamps (365 nm wavelength). Both hydrophilic (AAm, DMMSA) and hydrophobic (OFA, BA, STY) monomers were chosen in trials (Scheme 1). One gram of the 2EtAQ dyed cotton fabric was dipped into a monomer solution with concentrations varied from 2% w/v to 30% w/v, and then was padded. The wet pick-up rate of all samples was controlled around 100%. Then the padded fabrics were placed in sealed transparent boxes under either aerobic or anaerobic atmosphere, and irradiated under UVA light (365 nm) for different durations. The distance between the lamp and the samples was 12 cm, with light intensity measured as 3 mW/cm^2. Finally, all samples were rinsed vigorously with water, acetone or acetone plus toluene to remove all unreacted monomers and homopolymers. The grafting efficiency was evaluated on the basis of gravimetric method, shown in the following equation:

$$\text{Grafting efficency} = \frac{W_1 - W_0}{W_1 - W_0} \times 100\% \quad (1)$$

where W_0 is the mass of fabric before grafting, the W_1 is the mass of fabric after grafting and drying, and the W_2 is the mass of fabric after monomer loading and drying. All samples were conditioned in a standard environment for 24 h before weight measurements.

2.4. Characterization

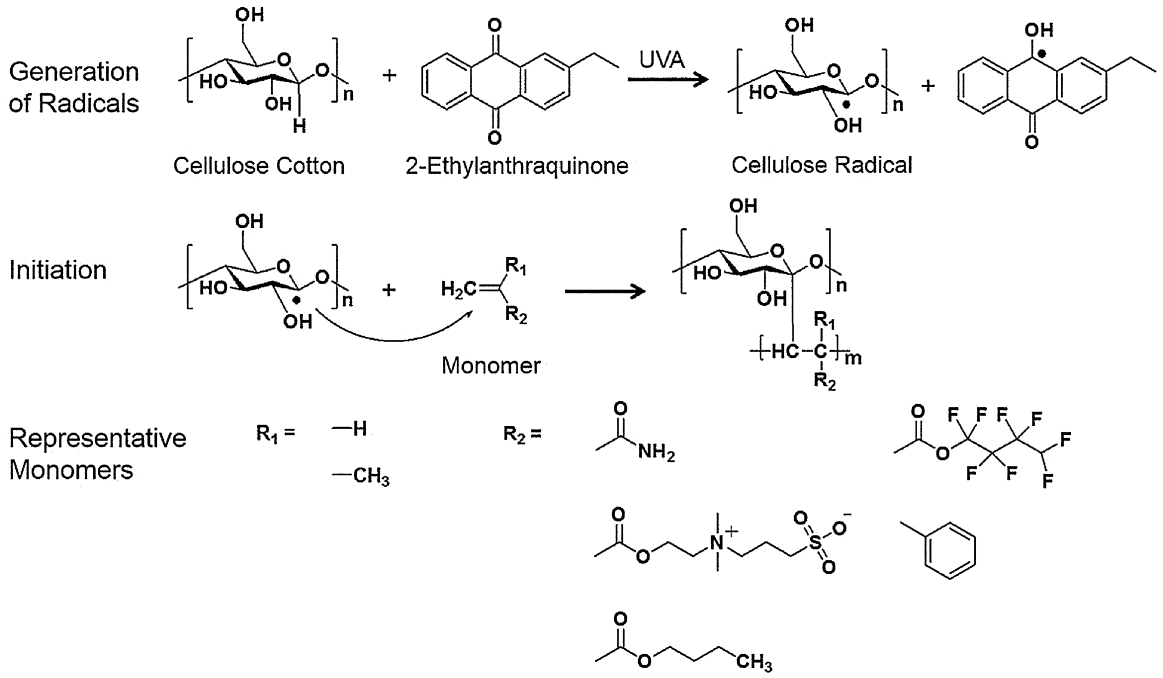
The amounts of 2EtAQ incorporated on cotton fabrics were determined by an extraction method. Treated samples were immersed in acetonitrile and shaken for 48 h in a dark environment. The concentrations of 2EtAQ in extraction solutions were measured with a UV–vis spectrophotometer (Evolution 600, Thermo Scientific) at 256 nm according to a calibration. Each result was an average of three parallel experiments.

Fourier transform infrared (FTIR) spectroscopy measurements of all samples were carried out with a Nicolet 6700 FTIR spectrophotometer (Thermo Electron Co., USA) with a resolution at 4 cm^{-1}, and 64 accumulations. Morphologies of both grafted and control samples were observed with a scanning electron microscope (SEM) (XL 30-SFEG, FEI/Philips, USA) at 5 kV accelerating voltage on gold sputter coated samples.

Thermogravimetric analysis (TGA) of all samples were conducted with a Shimadzu TGA-50 apparatus (Shimadzu Scientific Instruments Inc., USA) with a heating rate 10 °C/min from 30 °C to 500 °C under nitrogen atmosphere.

2.5. Antibacterial assessment

Light-induced antimicrobial activities of all samples were evaluated against bacterial strains *Escherichia coli* (*E. coli*) (K-12), and



Scheme 1. Proposed reaction mechanism of light-induced graft polymerization on 2EtAQ dyed cotton fabrics.

Staphylococcus aureus (*S. aureus*) (ATCC 12600) according to a modified AATCC testing method 100. *E. coli* and *S. aureus* were incubated in nutrient broth and tryptic soy broth, respectively, at 37 °C for overnight (18–24 h), then the cultures of the midexponetial-phase bacterium were diluted with phosphate buffer saline (PBS) to approximately 10^5 CFU/mL for later use.

Two pieces of $3 \times 3\ cm^2$ swatches of pristine cotton, 2EtAQ dyed and grafted fabrics were placed in separated sterile petri dishes and inoculated with 300 μL diluted bacterial suspension, respectively. All samples were exposed to UVA (365 nm) light for 60 min in the UV-crosslinker, while control samples were covered and stored in dark environment for the same duration. Afterward, the fabrics were soaked in 30 mL of sterilized PBS solution, and then the mixture was shaken vigorously for 1 min. An aliquot of 0.1 mL of the mixture solution was taken out and diluted to 10, 10^2, 10^3 and 10^4 in series, then placed on an agar plate. After incubation at 37 °C for 18 h, the reduction rate of bacteria was calculated based on the numbers of colony forming units on agar plate:

$$\text{Reduction rate of bactoria } (\%) = \frac{B - A}{B} \times 100 \quad (2)$$

where B is the number of colony forming units of controls (without light exposure) and A is the number of colony forming units of light exposed samples.

3. Results and discussions

3.1. Preparation of 2EtAQ dyed cotton fabrics

2-Ethylanthraquinone was incorporated onto cotton fabrics through a controllable vat dyeing process with sodium dithionate as a reducing agent and O_2 as an oxidizing agent. After the reduced 2EtAQ was completely oxidized back to the original structure, the fabric samples were washed thoroughly in boiling soap solution to remove all auxiliary and unfixed chemicals. The amount of 2EtAQ incorporated onto one gram cotton fabric through the dyeing process was examined by the extraction test, and results are shown in Fig. 1. It is clear that the quantity of 2EtAQ incorporated onto the fabric samples increased linearly with raised concentrations of 2EtAQ in dyeing baths. The cotton fabric, however, became gradually saturated with the chemical concentration reached 6% owf, which can be observed in the flattened change on the amounts of 2EtAQ loaded onto the fabrics treated in 6% and 9% owf baths. However, only small amounts of the photosensitizer were fixed on the cotton fabrics after the dyeing process due to the low substantivity of 2EtAQ to cellulose fibers.

3.2. Light-induced graft polymerization on 2EtAQ dyed cellulose

Vinyl monomers can be grafted onto cotton fabrics via UVA-initiated free radical polymerization in the presence of the photosensitizer, 2-ethylanthraquinone (2EtAQ). The proposed light-induced grafting mechanism is shown in Scheme 1. Upon exposure to UVA light, 2EtAQ is excited to its singlet state which can go through ultrafast intersystem crossing to its triplet state (Ramesdonk et al., 2006). The triplet 2EtAQ would be able to

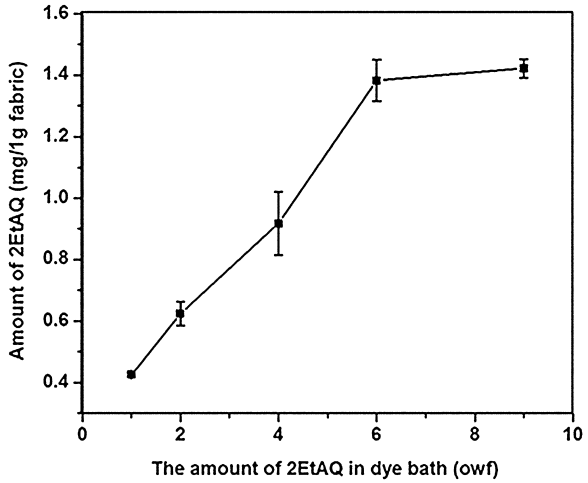


Fig. 1. Quantification of 2EtAQ on cotton fabrics treated with different concentrations, 1–9% owf.

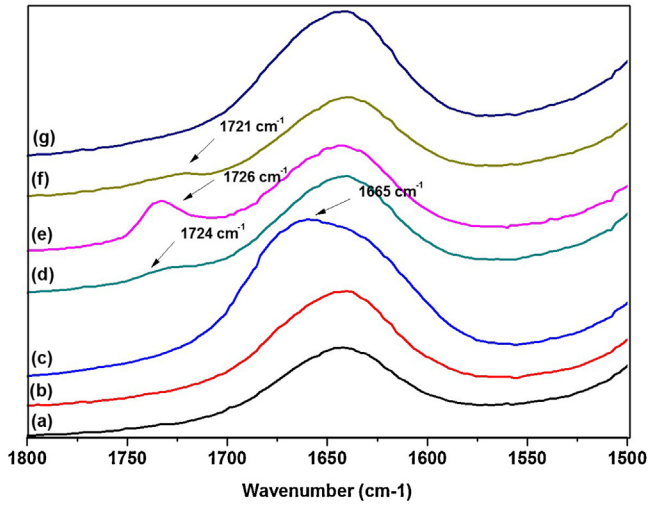


Fig. 2. FTIR spectra of (a) pristine cotton, (b) 6% owf 2EtAQ dyed cotton, (c) polyAAm grafted cotton, (d) polyDMMSA grafted cotton, (e) polyBA grafted cotton, (f) polyOFA grafted cotton and (g) polySTY grafted cotton. Concentration of monomer solutions was 10% w/v. UVA irradiation time was 1 h.

abstract hydrogen directly from cellulose chains, generating cellulose and anthraquinone radicals which can subsequently react with vinyl monomers. The most vulnerable hydrogen to be abstracted in cellulose structure is the one at 1-position (Liu & Sun, 2008), which is the most active one in the glucose ring. The ketyl radials formed from 2EtAQ is less reactive than the polymer radical toward monomers due to the high steric hindrance, and served mostly as terminators in the graft polymerization.

Formations of grafted polymers on the surface of cellulose fibers can be evidenced by Fourier transform infrared spectroscopy (FTIR) analyses, shown in Fig. 2. All samples showed a broad peak around 3400 cm^{-1}, assigned to the inter- or intra-chain hydrogen bonds in the cellulosic structure, and an intense peak at 1640 cm^{-1}, attributed to vibrational mode of absorbed water in cotton fabrics. No significant structural change was detected on 6% owf 2EtAQ dyed cotton due to the small amount of the chemical incorporated on it. On the other hand, noticeable characteristic peaks of functional groups of the monomers were observed on the grafted materials, except for the one grafted with styrene. In the cases of the monomers containing ester groups, such as [2-(methacryloyloxy) ethyl] dimethyl-(3-sulfopropyl) ammonium hydroxide, butyl acrylate, and 1*H*,1*H*,5*H*-octafluoropentyl acrylate, the peak of 1724 cm^{-1} or 1721 cm^{-1} representing the ester bond (—COO—) can be observed, and the peak intensities are varied according to different grafting yields. A clear peak shifting was detected on acrylamide-grafted-cotton from 1640 cm^{-1} to 1665 cm^{-1}, which is corresponding to the —C=O— stretching (amide band I), revealing polyacrylamide grafted onto the cotton fabrics.

Surface morphologies of pristine cotton, 2EtAQ treated cotton and grafted samples were examined with a scanning electron microscope (SEM), and are shown in Fig. 3. No significant morphological change was observed on the 2EtAQ dyed fabric. Noticeable morphological changes, however, were observed on the surfaces of the cellulose fibers after light-induced grafting under 1 h UVA irradiation in anaerobic atmosphere, depending on the types of monomers and the grafting efficiency. Coatings and fibrils of polyacrylamide were found on the top of cellulose fibers grafted with 10% w/v acrylamide. By increasing the concentration of monomer solutions, the coating of the polymer became wider and coarser, covering most area on fiber surfaces (Fig. 3c inset image). Thin ribbon shaped polymers were found on 1*H*,1*H*,5*H*-octafluoropentyl acrylate and butyl acrylate grafted fibers. It is interesting to observe that significant amount of small particles appeared on the surface of the cotton grafted with [2-(methacryloyloxy) ethyl] dimethyl-(3-sulfopropyl) ammonium hydroxide (Fig. 3d). The results indicated that the radical graft polymerization of four different monomers was successfully initiated by exposing the 2EtAQ dyed cotton fabrics to UVA light. And the grafting efficiency and polymer morphologies varied by different monomers.

3.3. Light-induced grafting with styrene

Styrene was also attempted to be grafted onto the dyed cotton fabrics through the same process, but failed. No new peak was observed in the spectrum of the styrene grafted cellulose fibers (Fig. 2g) after 1 h UVA light exposure. Additional studies found that even no homopolymerization of styrene was observed in a solution system containing styrene monomer, 2EtAQ and a good hydrogen donor, isopropanol under nitrogen protection, after 1 h UVA irradiation. The results further suggested that the polymerization of styrene could not be initiated by the excited 2EtAQ.

This observation is consistent with previous reports revealing that styrene could act as a quencher of triplet excited state of benzophenone chromophore with a decaying rate $k_q = 3.1 \times 10^9$ $(M\,s)^{-1}$ through a triplet-triplet energy transfer process (Tasis, Siskos, & Zarkadis, 1998; Wardle, 2009). The high triplet state energy of ketones and a close singlet state energy of styrene enhanced the feasibility of this quenching process (E_T of benzophenone = 289 kJ/mol, and E_S of styrene = 260 kJ/mol) (Tasis et al., 1998). Considering the similar photo-activity of benzophenone and 2EtAQ as well as the triplet state energy of 2EtAQ (E_T = 265 kJ/mol) (Lin & Aue, 1999), a similar decay of the triplet anthraquinone could be expected in this system. In addition, the decaying rate of this system may be higher than the benzophenone system since the triplet state energy difference between styrene and 2EtAQ is only around 5 kJ/mol, much lower than the difference between styrene and benzophenone derivatives. Therefore, the triplet anthraquinone could be significantly quenched by the excited styrene, affecting the hydrogen abstraction and subsequent reactions.

3.4. Controllability of graft polymerization

The grafting efficiency of light-induced free-radical polymerization of acrylamide was investigated against the reaction atmosphere (aerobic or anaerobic), the photo-sensitizer concentration, amount of monomer, and light irradiation duration, and results are shown in Fig. 4.

The effect of O_2 on the light-induced polymerization was examined by exposing acrylamide padded 2EtAQ dyed cotton fabric under UVA light in the air or in the laminated condition, shown in Fig. 4a. No weight change of the cotton fabrics was observed after the graft polymerization in O_2 environment after 1 h UVA irradiation. However, the grafting yield was significantly raised by replacing O_2 with N_2, indicating oxygen is an inhibitor to the radical-polymerization reactions. The results are consistent with previous results demonstrating that the molecular oxygen significantly impedes the generation of the radicals and initiation steps of the polymerization (Chong, 1969; Decker & Jenkins, 1985; Green, 2010; Ligon, Husar, Wutzel, Holman, & Liska, 2014; Yagci et al., 2010). According to photo chemistry, the lowest triplet state (T_1) of 2EtAQ could be quenched by the ground state oxygen (also T_1) through an energy transfer process. Moreover, the cellulose-macroradicals (Scheme 1 cellulose radical) resulted from the initiation process may also be quenched, reducing the active sites in the backbone. Consequently, the presence of the molecular oxygen could reduce the rate and the degree of polymerization significantly.

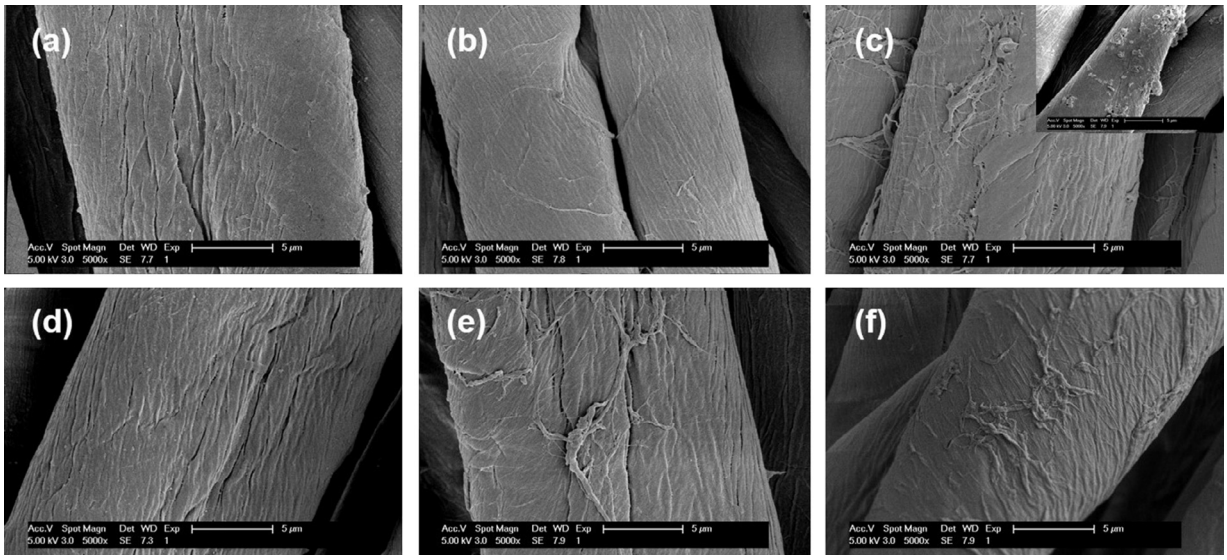


Fig. 3. SEM images of (a) plain cotton fiber; (b) 2EtAQ dyed cotton fiber (6% owf); (c) polyAAm grafted cotton fiber and inset in (c), polyAAm grafted cotton fiber with 30% w/v monomer concentration; (d) polyDMMSA grafted cotton fiber; (e) polyBA grafted cotton fiber (f) polyOFA grafted cotton fiber. Monomer concentration of all samples was 10% w/v. Samples were grafted under UVA for 1 h in anaerobic atmosphere.

Effect of the photo-sensitizer concentrations on acrylamide graft polymerization was evaluated on the dyed cotton fabric with different amounts of 2EtAQ after 1 h UVA irradiation (Fig. 4a). It was observed that the grafting efficiency was improved gradually as the number of the photo-sensitizer incorporated on cellulose increased. More active sites could be generated on the surface of cotton fibers upon light irradiation, leading to increased initiation reactions and polymerization. Meanwhile, the grafting efficiency increased initially with prolonged UVA exposure time up to 60 min, and afterward the increase in light irradiation would have less impact, showing a flattening effect from 60 to 80 min (Fig. 4b). The limited diffusion rate of the monomer in the system could lead to unchanged degree of polymerization beyond a particular duration, and also not enough free monomers left over on the surface of samples after long reaction time. Thus, a combination of factors leads to a flattened grafting efficiency by further increasing exposure duration.

The influence of the monomer concentration exhibited impact on grafting efficiency of acrylamide, shown in Fig. 4c. The cotton fabrics dyed with 6% owf 2EtAQ were padded with acrylamide monomer solutions with concentrations varied from 2% to 30% w/v. It is interesting to observe that the grafting efficiency increased from 11.8% to 38% by increasing the monomer concentration from 2% to 10% w/v, and then significant decreased to 25% while the concentration of monomer solution was further raised up to 30% w/v. When the concentration of the monomer was increased to a critical level, the amount of the monomer loaded on surfaces of the fabrics may block UVA and reduce radicals generated by the light, leading to low grafting efficiency. In addition, acrylamide monomer was also a good hydrogen donor due to the weak N—H bond in the structure. With high monomer concentration, the competition between two hydrogen donors, cellulose and acrylamide, was expected. The possibility for triplet 2EtAQ to abstract hydrogen from monomer was increased, resulting in high percentage of homopolymerization observed in the system, reducing the grafting efficiency.

3.5. Thermal properties of surface modified cellulose

The thermal stability of control and modified samples were determined by using thermal gravimetric analysis (TGA). Typical TGA profiles of the comparison of the control cellulose fiber, photosensitizer treated fiber and grafted materials are shown in Fig. 5a. Both the control and 2EtAQ dyed fibers were thermally stable up to ~350 °C, no influence on original properties from the dyeing process. The onset decomposition temperatures of the grafted cellulosic fibers were 311 °C, 334 °C, and 331 °C, respectively, corresponding to 10% w/v DMMSA, BA and OFA grafted fibers, while that of acrylamide grafted material was almost same to the control sample. The varied thermal stabilities of the samples can be attributed to thermal properties of the grafted polymers and the effect of grafting on the cellulosic materials.

The thermal stability of acrylamide grafted cellulose fibers was evaluated as the function of monomer concentrations in the treatment solutions (Fig. 5b), which are related to the amount of formed polyacrylamide on the surface. According to the results, the onset decomposition temperature and the thermal degradation residue of samples increased gradually with the increasing amount of the grafted polymer. Grafted polyacrylamide may form stable imide six member rings under elevated temperature, producing more residues as well (Grassie, Mcneill, & Samson, 1978; Minsk, Kotlarchik, Meyer, & Kenyon, 1974).

3.6. Light-induced antimicrobial activity of grafted cotton fabrics

According to the previous research (Zhuo & Sun, 2013), the 2EtAQ dyed cotton fabrics were able to provide light-induced antibacterial functions on materials due to the generation of reactive oxygen species (ROS) on cellulose under light exposure. In order to evaluate whether the grafted polymer on the surface would alter the antibacterial activity of the 2EtAQ dyed cotton fabrics, all samples were tested against *E. coli* (Gram-positive) and *S. aureus* (Gram-negative) according to a modified AATCC standard testing method 100. The pristine cotton, 2EtAQ dyed fabrics and the surface-grafted samples were inoculated with 10^5 CFU/mL bacterial suspension, and then illuminated under UVA light (365 nm) with a fluence dose of 3 mW/cm^2 for 60 min (equivalent to a fluence dose of 10.8 J/cm^2). The bacterial reduction rates are shown in Table 1. According to the experimental results, the 2EtAQ dyed cotton did not show any noticeable antimicrobial properties, similar to the control samples without light irradiation. All 2EtAQ dyed cellulose and surface-grafted samples with different monomers provided powerful antibacterial activities against both *E. coli* and *S. aureus* under the UVA irradiation.

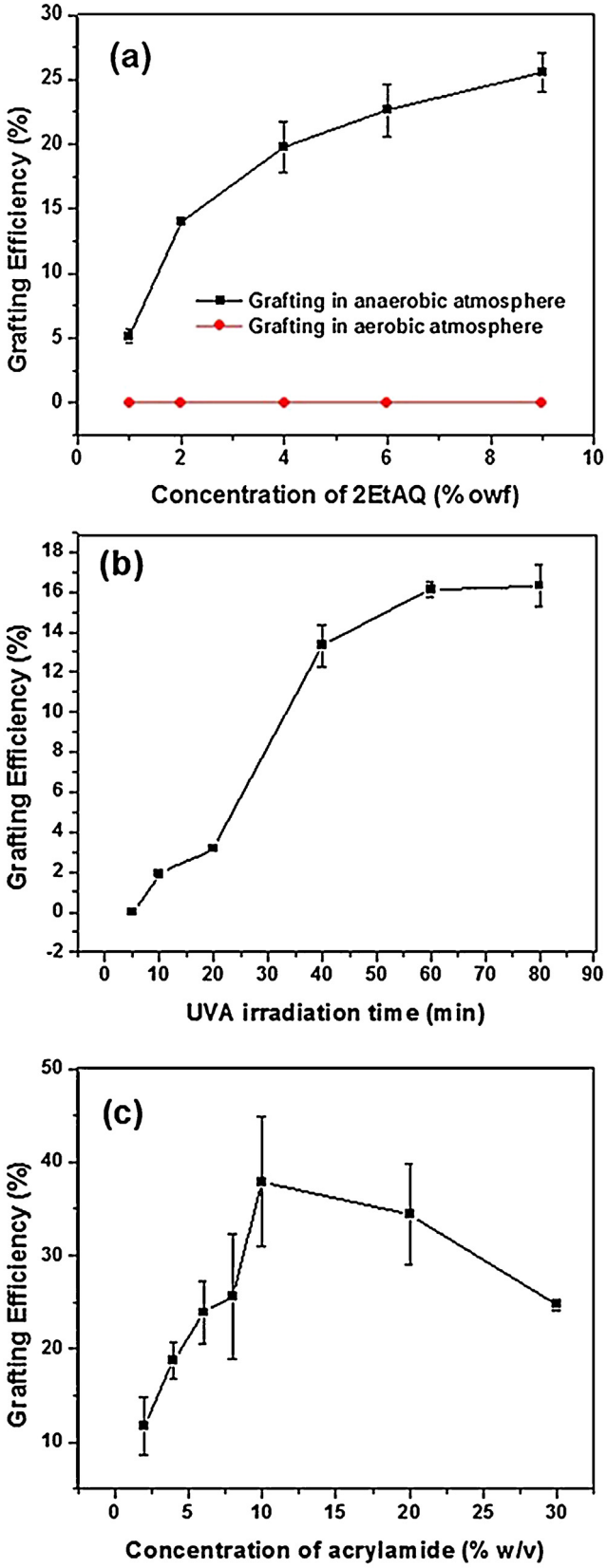


Fig. 4. (a) Effects of atmosphere and concentration of photo-sensitizer on polyacrylamide grafting efficiency on cotton fabrics; 8% w/v acrylamide, 1 h grafting time. (b) Effect of grafting time on polymerization efficiency on cotton fabrics, 8% w/v acrylamide, 6% owf 2ETAQ. (c) Effect of monomer concentration on polyacrylamide grafting efficiency on cotton fabrics; 6% owf 2EtAQ, 1 h grafting time.

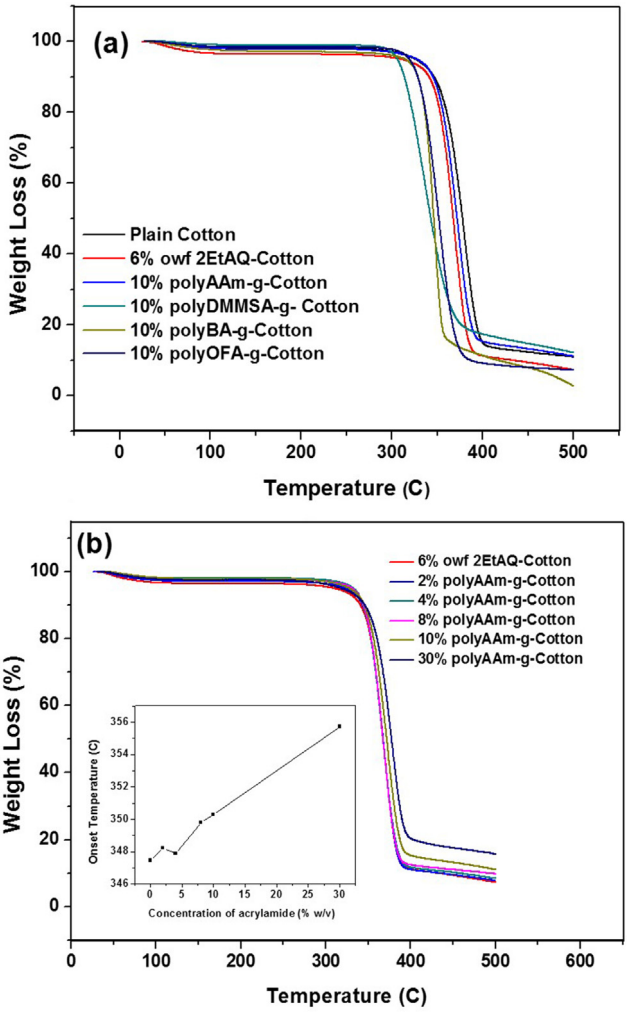


Fig. 5. TGA curves of (a) pristine cotton, 2-ethylanthraquinone dyed cotton and grafted cotton fabrics; (b) polyacrylamide grafted cotton with monomer concentration from 2% to 30% w/v. For inset figure, the relationship between onset temperature (°C) and concentration of acrylamide from 0% to 30%.

Table 1
Light-induced antimicrobial functions of vat dyed and grafted cotton fabrics, and the concentration of free 2-ethylanthraquinone on the fabrics.

Samples	Reduction rate of bacterial count (%)		Amount of 2EtAQ extracted from materials (mg/(1 g) fabric)
	E. coli (10^5 CFU/mL)	*S. aureus* (10^5 CFU/mL)	
Plain cotton	0.00	0.00	0
6% owf 2EtAQ cotton	99.99	99.99	1.45
PolyAAm-*g*-cotton[a]	99.99	99.99	1.36
PolyDMMSA-*g*-cotton[a]	99.99	99.99	1.38
PolyOFA-*g*-cotton[b]	99.99	99.99	1.32
PolyBA-*g*-cotton[b]	99.99	99.99	1.34

Concentration of 2-ethylanthraquinone is 6% owf. UVA exposure time is 1 h.
[a] Monomer concentration is 10% w/v in DI water.
[b] Monomer concentration is 10% w/v in acetone or acetone plus toluene.

The surface graft polymerization process and the presence of different grafted polymers on the fiber surface did not shield the light-induced functions. The excellent antibacterial activity showed that the incorporated 2EtAQ structures were still photo-active, capable of generating sufficient amount of reactive oxygen species and deactivating all bacteria in the environment. Anthraquinone compounds contain two carbonyl groups which can undergo the photo-activation processes and provide light-induced functions, respectively, a potential advantage versus photo-active benzophenone compounds.

According to an extraction test, in which 2EtAQ dyed and all grafted samples were immersed in acetonitrile and shaken for 48 h, the amount of free 2EtAQ on the ungrafted and grafted samples were in the same range, indicating that no significant amount of anthraquinone was consumed during the graft polymerization. The extracted 2EtAQ was basically unchanged, meaning that most of the photosensitizer did not add to monomers or covalently bond inside the grafted polymers. A possible reason is that the anthraquinone ketyl radical has steric resistance for radical addition reaction.

4. Conclusions

A novel and effective photo-induced graft polymerization was successfully conducted on the surface of 2EtAQ dyed cotton fabrics. 2EtAQ serves as an efficient photosensitizer and initiates radical polymerization reactions under UVA irradiation. Compared with existing photo-initiated surface grafting methods, this vat dying and photo-grafting process is more practical and environmentally friendly. The successful surface graft polymerizations of four different monomers were confirmed on the 2EtAQ dyed fabrics by using FTIR and SEM analyses. No significant grafting of styrene was detected on the fibers due to the quenching effect of styrene to the initiator. In addition, the grafting efficiency of monomers could be controlled by the amount of the photosensitizer, existence of molecular oxygen, the concentration of monomer solution and the photo-irradiation time. The thermal stabilities of cellulose were slightly changed after graft polymerization depending on the types of monomers. Both 2EtAQ dyed cotton fabrics and grafted samples demonstrated light-induced antimicrobial effects against both Gram-negative and Gram-positive bacteria.

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