Surface Grafting of Paper with Photochromic Spiropyran Ether Methacrylate

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It was demonstrated that a photochromic paper could be made through the atom transfer radical polymerization (ATRP) method by grafting spiropyran ether methacrylate (SPMA) onto the fiber surface. The surface composition and topography of the grafted paper were analyzed by Fourier Transform Infrared Spectroscopy (FTIR), X-ray photoelectron spectra (XPS), and scanning electron microscopy-energy dispersive spectrometer (SEM-EDS). Crystal structures of the cellulosic fibers were also examined after the grafting reaction. The characteristic absorption bands detected in the FTIR spectrum after grafting suggested that a new functional group was formed by the reaction. The XPS and SEM results confirmed that SPMA was grafted onto the surface of the fibers successfully. The grafted spiropyran groups exhibited reversible photochromic properties when exposed to UV light irradiation and visible light. The modified paper showed a purple color under UV light irradiation and changed back to its original color when exposed to visible light. This surface modification using ATRP was demonstrated to be a feasible way to prepare photochromic paper.

Keywords: ATRP; Surface grafting; Photochromic paper; Spiropyran ether methacrylate

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INTRODUCTION

Paper, a major participant in culture and information exchange, has played an important role for thousands of years. Due to its light weight, high flexibility, low cost, good chemical and physical stability, and good ink adsorption under atmospheric conditions, it can be regarded as the best medium for such purposes.

Produced from plants, cellulosic fiber is the main component of paper. In the past, studies on functional cellulose fibers have increased in areas such as biosensors, electronics, and batteries (Rogers *et al.* 2001; Xiao *et al.* 2012; Edwards *et al.* 2013; Huang 2014; Xu *et al.* 2014). Photochromic paper changes color upon irradiation with UV light, which is a good property for document identification and can be applied for security and authentication purposes.

Photochromism is a reversible interconversion between two states effected by irradiation (Klajn 2014; Irie 2000; Zhu *et al.* 2010). The main photochromic compounds include spiropyrans (SP), spirooxanines (SO), and diarylethenes. Spiropyrans will isomerize when excited by ultraviolet light, and the structure of colourless spiropyran (SP) changes to colored merocyanine (Mer). Once the Mer structure is exposed to visible light, it reverts to SP (Hirakura *et al.* 2004; Wang *et al.* 2014a). Spiropyran-based materials have been widely applied in many fields, such as data storage, optical and electrical switching, and signal transduction (Ivashenko *et al.* 2013; Renkecz *et al.* 2013; Sun *et al.* 2013; Wang *et al.* 2014a). Introducing SP compounds onto the surface of a substrate can produce light-responsive material.

The main difficulties in the production of photochromic paper are generally related to the adhesion ability of the photochromic dye onto the pulp fibers. The low water solubility of a photochromic dye causes its low adsorbing capacity. In addition, poor compatibility between pulp fibers and photosensitive chemical fibers will lead to inter-pulp aggregation.

There are many preexisting studies on improving the adhesion of a photochromic dye onto pulp fibers. For example, Billah *et al.* (2012) tried to improve adhesion by introducing hydrophilic groups to the photochromic dye to improve its water solubility. This provided a new coloring method for photochromic acidic dyes to be applied to wool for improved coloration. Coating, a processing technology after the papermaking process, can also impart some special properties to paper. Sun *et al.* (2013) applied photochromic latex on cellulose paper, imparting the paper with photochromic characteristics.

Chemical modification of fiber plays a significant role in the papermaking industry. Chemically modified cellulosic papers can have special functional properties, such as hydrophobicity, biofunctionality, and electrical conductivity (Samyn 2013; Aubrecht *et al.* 2015; Yagyu *et al.* 2015). Also, security paper can be made using chemical modification, such as ATRP. One of the interesting applications of ATRP is surface grafting, which is an important chemical medical technology.

In this work, photochromic spiropyran ether methacrylate (SPMA) was grafted onto filter paper to give it photochromatic characteristics. The photochromatic performance of the paper was evaluated using visible light and UV light irradiation for several cycles. The surface composition and morphology of the modified paper were analyzed by FTIR, XPS, and SEM.

EXPERIMENTAL

Materials

The photochromic spiropyran ether methacrylate (SPMA) monomer was prepared according to our previously reported methods (Wang *et al.* 2014b). Briefly, SPMA produced from esterification of carboxyl-containing spiropyran (SPCOOH) / hydroxyethyl methylacrylate (HEMA) at a molar ratio of 1:1 in tetrahydrofuran. SPMA was obtained after separation and purification.

CuBr (97%; Acros) was purified by stirring with acetic acid and washed with methyl alcohol three times, until the washings became clear. The CuBr was then dried in a vacuum oven at 50 °C for 48 h. 2-Bromoisobutyryl bromide (BiBB, 98%), tris (2-(dimethylamino) ethyl) amine (Me_6-TREN, 99%), 2-ethyl bromoisobutyrate (EBiB, 98%), 4-(dimethylamino) pyridine (DMAP, 99%), and trimethylamine (TEA, 99%) were used as received from Acros (Acros, Innochem Science & Technology Co., Ltd. China). Tetrahydrofuran (THF; Sigma, 99.9%) was dried overnight over CaH_2 and distilled under reduced pressure before use.

Water (18.2 MΩ) was purified with a Millipore Milli-Q system (Millipore Direct-Q5, Merck, America). All other chemicals were of analytical reagent grade and used without further purification. UV and visible light irradiation were conducted with 8-W UV (354 nm) and white light (620 nm) lamps.

Immobilization of the ATRP Initiator on Cellulosic Paper (fiber initiator)

The procedure was adopted from Lindqvist *et al.* (2008). Filter paper (Xinhua Paper Industry Co., Ltd. Hangzhou, China) was cut into specimens 40×40 mm in size and was extracted using acetone and tetrahydrofuran, respectively, prior to use. The filter paper, 3.6 mL of TEA (2.46×10^{-2} mol), a catalytic amount of DMAP, and 100 mL of dry THF was added into a round-bottomed flask. Then, 3.20 mL of BiBB (2.46×10^{-2} mol) was added, drop-wise, to the mixture in 5 min. The reaction proceeded for 24 h at room temperature on a shaking device. The filter paper was then thoroughly rinsed and ultra-sonicated in dichloromethane (CH_2Cl_2) and ethanol to remove any non-grafted Br-initiator from the filter paper.

Grafting of Spiropyran Ether Methacrylate (SPMA) from Initiator-Functionalized Filter Paper

A certain amount of fiber initiator, SPMA, Cu(I)Br, Me_6-TREN, and 2-ethyl bromoisobutyrate (EBiB) were immersed in a flask with ethyl acetate (50 mL). The flask was degassed with Ar gas three times and sealed with a rubber septum. The polymerization was carried out in the dark at 35 °C for 18 h. The resulting products were subjected to thorough rinsing with THF, THF:water (1:1), water, and CH_2Cl_2, and finally dried in a vacuum oven at 35 °C.

SPMA conversion is calculated according to Eq. 1,

$$\text{Conversion} = \frac{W_2 - W_1}{W_{SPMA}} \times 100\% \qquad (1)$$

where W_1(g), W_2(g), and W_{SPMA}(g) are the weight of fiber initiator, fiber graft copolymers, and the addition of monomer, respectively.

The weight average molecular weight of the PSPMA grafted on fiber was determined by gel permeation chromatography (GPC; Agilent 1100, USA)

Fourier Transform Infrared Spectroscopy (FTIR)

Fourier transform infra-red (FTIR) spectra of samples were acquired on a Nexus 470 spectrophotometer (Thermo Nicolet, USA). The dry samples were mixed and ground with KBr and then measured in the wavenumber range of 400 to 4000 cm^{-1}.

X-ray Photoelectron Spectra

X-ray photoelectron spectra (XPS; Kratos Axis Ultra DLD, Japan) were recorded by Mg Kα (1253.6 eV) monochromatic X-ray source (Kratos Axis Ultra, UK). Binding energies were calibrated using the signal of C1s as reference energy (C1s = 284.6eV).

X-Ray Diffraction Analysis

X-ray diffraction (XRD) diffractograms were collected using a D8 ADVANCE diffractometer (Bruker, Germany) equipped with a Cu Kα monochromatic radiation (λ = 0.154 nm) generated at a voltage of 40 kV and a current density of 40 mA. The samples were scanned at 2θ = 10° to 40°. The crystalline index (I_{CR}) was computed from the XRD patterns using the following equation,

$$I_{\text{CR}} = 1 - \frac{I_{\text{AM}}}{I_{002}} \qquad (2)$$

where I_{AM} is the amorphous part reading at 18° and I_{002} is the counter reading at the maximum (at 22°).

Scanning Electron Microscopy (SEM)

Samples were observed using a Merlin Scanning Electron Microscope (ZEISS, Oberkochen, Germany) at an acceleration voltage of 25 kV. The samples were mounted on an aluminum stub using double-sided tape and coated with Au (JEOL JFC-1600 Auto Fine Coater, Japan) under a vacuum prior to analysis. The element compositions of grafted paper were measured on EDS (Oxford Instruments, UK) using X-MaxN20 double detector system.

RESULTS AND DISCUSSION

Atom transfer radical polymerization (ATRP) is a useful technique for grafting functional groups onto the surface of cellulosic fibers. It can convert more available hydroxyl groups to α-bromoesters, which are effective initiators for ATRP. The synthetic route is shown in Fig. 1. The grafting reaction condition was as follows: cellulosic paper in the solid state, SPMA monomer in the liquid state.

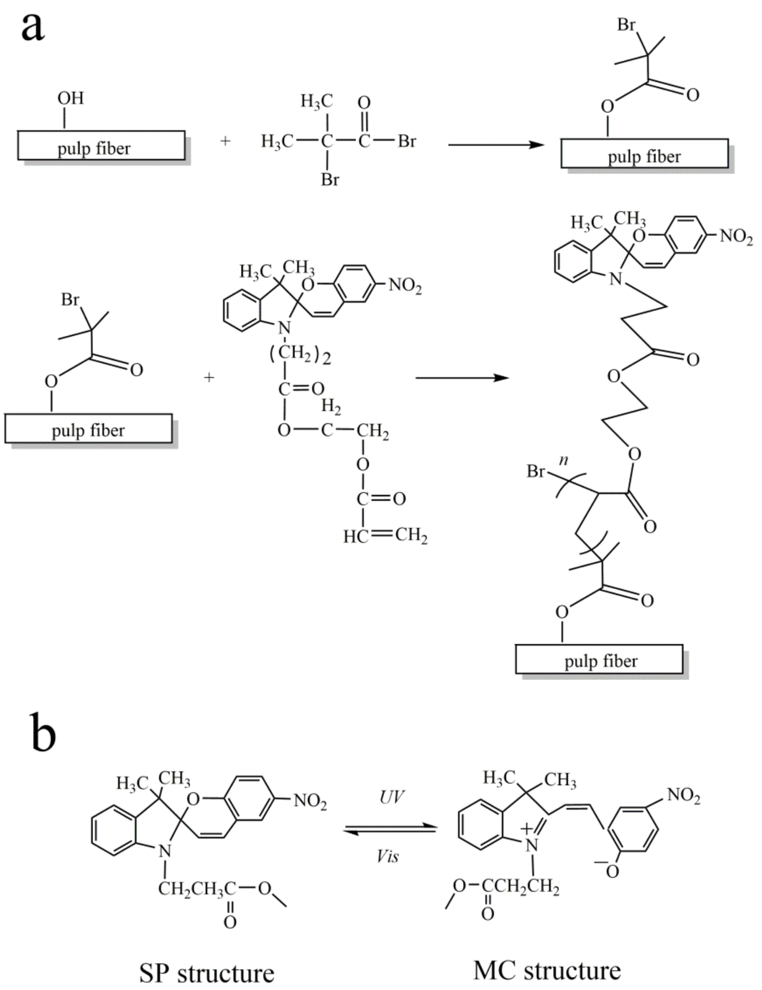


Fig. 1. Schematic representation of (a) the synthesis of SPMA-grafted on the cellulose fibers and (b) the photochromic process

FTIR of Modified Cellulosic Paper

Results of Fourier transform infrared spectroscopy (FTIR) analysis are shown in Fig. 1. In this case the fiber initiator was the macroinitiator and the target product of fiber-g-PSPMA was produced though ATRP. The FTIR spectra of the filter paper fiber are presented in Fig. 2a. The absorption peaks in the region near 3500 cm^{-1} indicate the stretching of hydrogen–bonded OH groups. The vibration absorption peaks near to 2900 cm^{-1} can be ascribed to C-H stretching vibration. A new band at 1750 cm^{-1} in the fiber initiator spectrum (Fig. 2b) is attributed to the carbonyl group that was formed during the esterification reaction. The key features that could confirm the successful surface modification are shown in Fig. 2c. The appearance of new absorption bands at 1510 and 1330 cm^{-1} can be attributed to the nitro group of the SPMA structure. Similarly, peaks at 1160 and 1480 cm^{-1} are characteristic absorptions of C–H in indoline C_3 and the spiro-heterocycle (C–O–C) of the fiber-g-PSPMA.

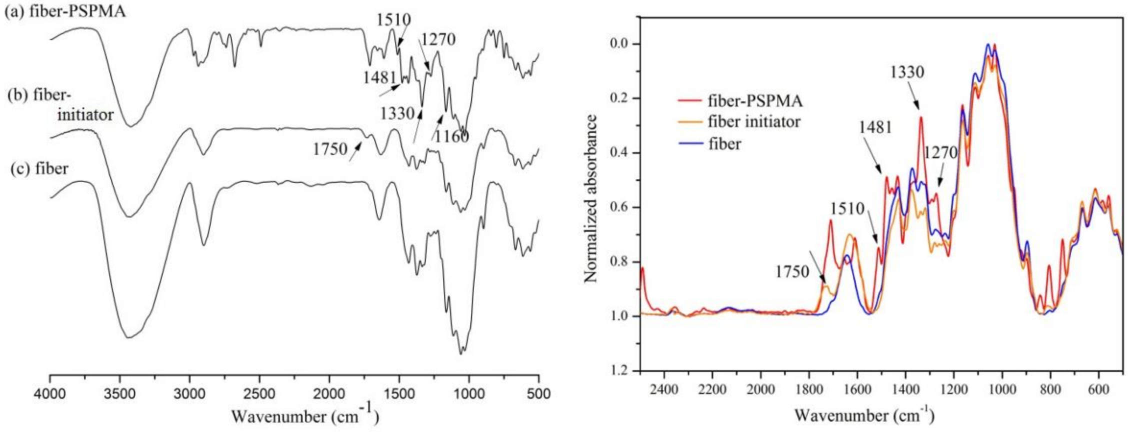


Fig. 2. FTIR spectra of (a) fiber (unmodified paper), (b) fiber initiator, and (c) fiber-g-PSPMA. The spectra were normalized so that the peak heights of the bands were equal

Surface Morphology and Chemical Composition Analysis

The SEM micrographs of unmodified paper, fiber initiator, and fiber–g–PSPMA are shown in Fig. 3.

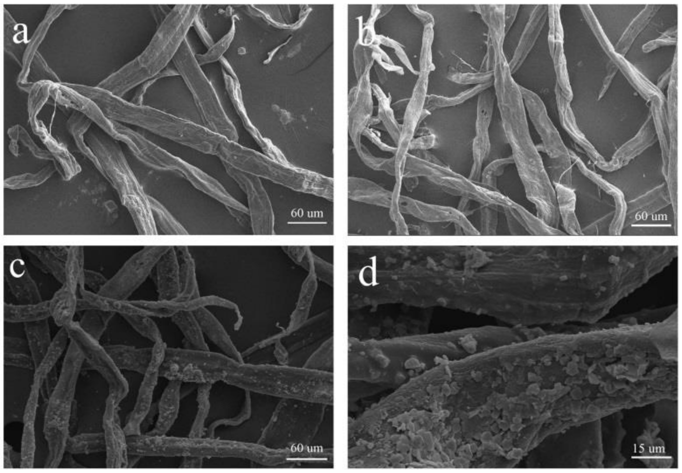


Fig. 3. SEM micrographs of (a) unmodified paper fiber×250, (b) fiber initiator×250, (c) fiber–g PSPMA×250, and (d) fiber–g–PSPMA×1000

Unmodified fibers showed a smooth and uniform surface, with some apparent folds caused by drying in the papermaking process. Compared with the unmodified fibers, a clear difference could be observed in the modified fibers. A thin layer was formed on the surface of fiber initiator, which resulted from the immobilization of the initiator BIBB. A noticeable amount of polymer matter can be found on the surface of fibers after the grafting reaction (Fig. 3c, d). This indicates that the SPMA was successfully grafted onto the fiber surface in the ATRP reaction. The results were also in agreement with the FTIR results.

X-ray photoelectron spectroscopy (XPS) is a surface-sensitive technique that can provide elemental composition information of a sample for a depth of a few nanometers as well as the chemical composition changes during the ATRP reaction. The XPS spectra of filter paper fiber, fiber initiator, and fiber–g–PSPMA are shown in Fig. 4. There are two emission peaks in the XPS spectrum of unmodified fiber (Fig. 4a). The peak at 284 eV is related to the binding energy of C 1s, and that at 531 eV can be ascribed to the binding energy of O 1s. The Br 3d peak (Fig. 4b) at 70 eV verified that fiber initiator can be used as a macroinitiator for ATRP reaction.

The surface compositions from XPS measurements are listed in Table 1. For the sample of fiber initiator, the composition of Br 3d rose from 0% to 2.03%, and C 1s increased while O 1s decreased. The results showed that the 2-bromoisobutyryl groups were introduced onto the fiber surface and fiber initiator was formed through an ester bond from the hydroxyl groups on the surface of fiber (Morsi *et al.* 2011).

The fiber–g–PSPMA spectrum (Fig. 4c) exhibits an N 1s emission peak at 402 eV, which is contributed by the SPMA nitrogen. The result confirmed the immobilization of PSPMA on the fiber surface. And also, there is a residual Cu content in the modified paper.

Table 1. Element Surface Composition Determined from XPS

Samples	Element surface composition (%)				
	C 1s	O 1s	N 1s	Cu 2p	Br 3d
Fiber	62.11	37.89	-	-	-
Fiber–initiator	67.56	30.42	-	-	2.03
Fiber–g–PSPMA	65.11	30.36	2.85	1.68	-

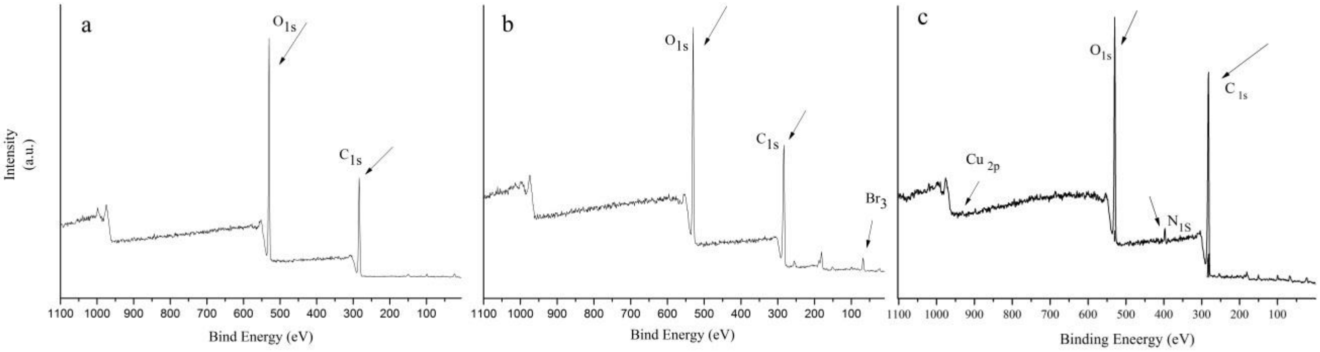


Fig. 4. XPS survey spectra of fiber, fiber initiator, and fiber–g–PSPMA

X-Ray Scattering

To study the influence of the chemical modification on the structure of the paper fiber, XRD measurements were performed for the fiber, fiber initiator, and fiber–g–PSPMA. Figure 5 shows the XRD diffraction and the crystallinity index. The XRD pattern for three samples clearly showed strong reflections (2*θ*) at approximately 16.5° and 22.6°, exhibiting cellulose-I X-ray patterns. The crystallinity index of fiber, fiber initiator, and fiber–g–PSPMA were 67.55%, 62.41%, and 61.83%, respectively. This indicated that the graft reaction occurred only at the surface of the fiber, and the structure of filter paper was not damaged during the reaction (Carlmark and Malmström 2003).

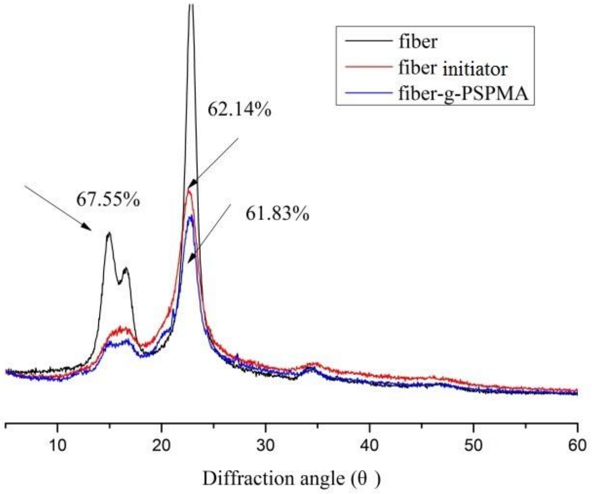


Fig. 5. X-ray diffraction of filter paper fiber, fiber initiator, and fiber–g–PSPMA

Analysis of PSPMA

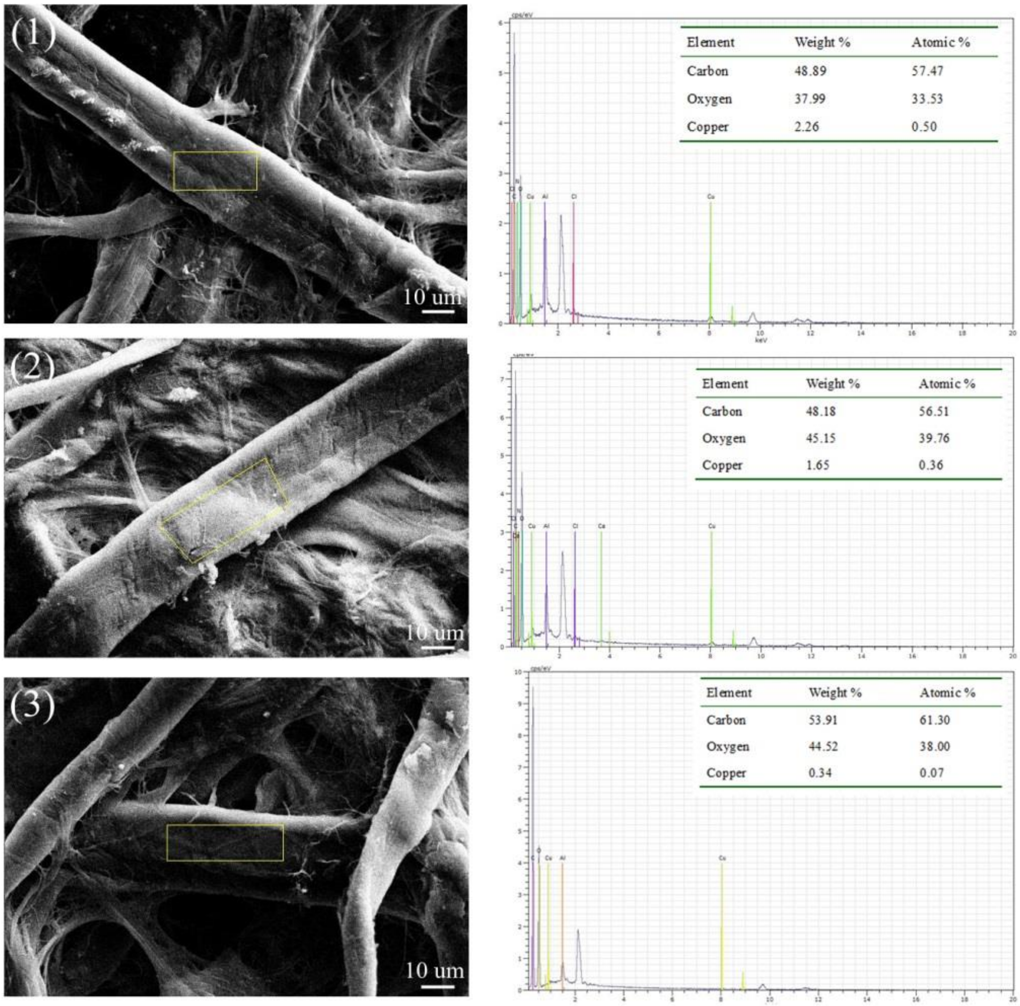
In this work, sacrificial initiators were added in the polymerization reaction to analyze the PSPMA on the fiber. Hence, polymerization reaction carried out both from the surface of fibers and the reaction system, which were triggered from fiber initiator and the sacrificial initiator. This method also used to assess the polymer grafted on the fiber surface (Carlmark and Malmström 2003). The grafted PSPMA were analyzed by GPC and the main result is listed in Table 2. Monomer conversions increased from 5.62% to 6.29% and 9.07% with increasing molar ratios of [SPMA]/ [fiber initiator] from 100:1 to 150:1 and 200:1. And the PDI of PSPMA became narrow. The results show that the polymerization is controlled.

Table 2. Experimental Data of ATRP of PSPMA Grafted onto Fiber

Entry	[SPMA]:[initiator]^a: [CuBr]:[(Me$_6$-TREN]	Temp. (°C)	Time (h)	Conv.^{b} (%)	M_n ^{c} (10^3 g/mol)	M_w/M_n	DP^d
1	100:1:1:1	30	6	5.62	5.1	1.40	14
2	150:1:1:1	35	12	6.29	9.7	1.30	26
3	200:1:1:1	30	18	9.07	29.4	1.15	69

[a] [initiator] is mole of bromine which is determined from XPS(M. Wang *et al.* 2013). [b] The SPMA conversion was calculated based on equation (1), [c] GPC was number average molecular weight (M_n) from free polymer which was triggered by sacrificial initiator (EBiB). [d] DP is the degree of polymerization of PSPMA, estimated from $M_w/M_{repeat\ unit}$ ($M_{repeat}=493$ g/mol).

To confirm the attachment of copper to the PSPMA-grafted fibers, EDS spectra was obtained to scan the component atoms of the entries listed in Table 2. Figure 7 shows the scanning area and elemental composition of C, O, and Cu. From the entries of (1), (2) and (3), it can be seen that Cu content showed a gradual decrement trend. This result demonstrated that more CuBr was consumed when promoted the proportion of [SPMA]:[CuBr].



Element	Weight %	Atomic %
Carbon	48.89	57.47
Oxygen	37.99	33.53
Copper	2.26	0.50

Element	Weight %	Atomic %
Carbon	48.18	56.51
Oxygen	45.15	39.76
Copper	1.65	0.36

Element	Weight %	Atomic %
Carbon	53.91	61.30
Oxygen	44.52	38.00
Copper	0.34	0.07

Fig. 6. Scanning area and the corresponding elemental mapping of different samples, (1) entry 1, (2) entry 2, (3) entry 3

Functional Performance of the Modified Paper

To explore the functional performance changes with the introduction of photochromic SPMA groups onto the fibers, the modified paper was exposed to light with different wavelengths. In this section, the investigation focuses on the photochromic effect of the modified paper using visible light and UV irradiation. Fig. 7 shows the color changes of the modified filter paper (entry 3). The color of the paper changed from colorless to purple after UV irradiation for 1 min (Fig. 7b). Then, the paper turned back to its original color upon irradiation with visible light for 5 min (Fig. 7c). Therefore, the coloration and de-coloration process are reversible.

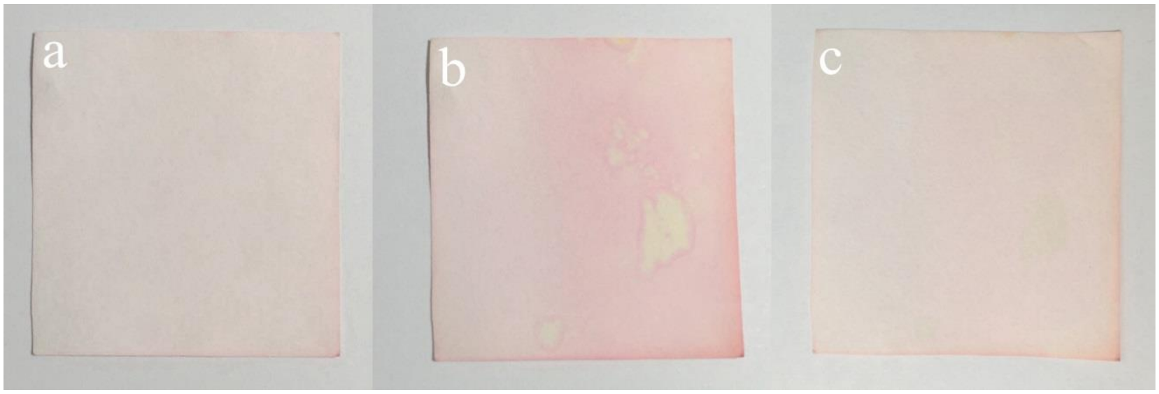


Fig. 7. Light responsive photochromic properties of modified filter paper (a) under visible light, (b) after irradiation with UV light for 1 min, and (c) under the visible light for 5 min

The observed photochromism in modified paper was related to the grafted SPMA. Spiropyran is a group of colorless, light-sensitive molecule that can absorb ultraviolet (UV) light. Under UV irradiation, the colorless, closed SP structure was isomerized to a merocyanine (MC) structure and showed color again. Exposure of the MC molecule to the visible light could revert it back to the SP structure, and the color could fade away, as shown in Fig. 7c. This process was a sign of the reversible conversion of purple MC to colorless SP.

Cyclic reversible response ability is an important parameter of photochromic materials for applications. Therefore, the cyclic ability of the paper was also evaluated. The sample was irradiated with UV light and visible light several times. The result showed that the reversible conversion could happen at the first several cycles. The results demonstrated that the PSPMA-grafted paper with the long chain length which has a degree of polymerization (DP) of 69 exhibited better photochromic behavior. However, for outdoor applications, future research should be carried out to improve the response ability with more cycles applied.

CONCLUSIONS

1. Photochromic paper was prepared by introducing photo-responsive spiropyran groups to the paper surface via ATRP. FTIR, XPS, and SEM observations revealed that SPMA was successfully immobilized on the fiber surface.
2. The XRD results indicated that the structure of filter paper was not damaged during the reaction
3. Irradiation with visible light and UV light were alternated, which showed that the modified paper exhibited photochromic properties. The results demonstrated that the PSPMA-grafted paper with a degree of polymerization (DP) of 60 exhibited better photochromic behavior. Therefore, the method on this paper might contribute to the basis for the development of a new special paper. Further work is needed to improve the cyclic reversible response ability of the photochromic paper.

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