

# Synthesis and Application of Polymeric Fluorescent Compounds Based on Coumarin

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In this work, a multifunctional yellowing inhibitor was synthesized by the Pechmann method. In order to obtain the target compound, 7-hydroxy-4-methyl coumarin was prepared by using the raw materials of resorcinol and ethyl acetoacetate, with toluene-p-sulfonic acid as the catalyst. New polymeric fluorescent compounds were synthesized by connecting the 7-hydroxy-4-methyl coumarin, the hindered amine light stabilizer 4-amion-2,2,6,6-tetramethylpiperidine, and a series of polyethylene glycol segments into the same molecule with cyanuric chloride as a bridge. The structures of the synthesized molecules were confirmed by FT-IR, <sup>1</sup>H NMR, and elemental analysis. The luminescent properties of the fluorescent compounds were studied by UV-vis spectroscopy and fluorescence spectroscopy. The integration effect between the fluorescent compounds and paper was tested by a scanning electron microscope. The light stability effect on the paper sheet was tested using an ultraviolet aging apparatus. The results indicate that the polymeric fluorescent compounds had a positive effect on the light stability of the high-yield pulp.

*Keywords:* 7-hydroxy-4-methyl coumarin; Fluorescent compounds; Light stability; High-yield pulp

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## INTRODUCTION

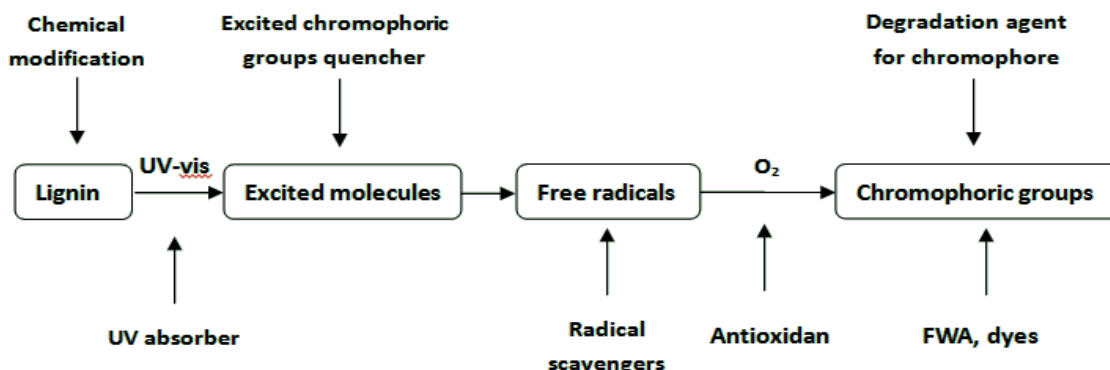
High yield pulp (HYP) products have found increased use in many paper grades, including printing and writing, coated and uncoated wood-free papers. HYP fibers exhibit clear advantages in applications requiring high bulk and opacity and good water absorbency. However, one of the main drawbacks that limit its more extensive applications is the photo yellowing tendency due to its high content of lignin and hemicelluloses (Zhang *et al.* 2009). Research has shown that the dosage of HYP could increase by 2 to 6 times if brightness loss was lessened to be within 3% during a period of 3 to 12 months (Connell and Cockram 2000).

Based on the research concerning the light-induced yellowing mechanism of HYP (Castellan *et al.* 1991; Paulsson and Parkas 2012), the different light-induced yellowing stages and proposed yellowing inhibition methods of HYP are shown in Fig. 1.

Methods aimed at inhibition of HYP yellowing inhibition are as follows: A) scouting the ideal bleaching method; B) modifying the lignin to increase its stability; C) adding chemical agents to inhibit or decrease the production of chromophoric groups; and D) destroying the chromophoric groups. Among them, adding chemical agents has been considered as the most feasible method.

Ultraviolet absorbents, radical scavengers, and fluorescent whitening agents can be used as yellowing inhibitors, and the effects have been demonstrated by various

researchers. The application of ultraviolet absorbers in paper industry has been limited by the poor water solubility and inefficient retention on the fibers. But they could contribute a beneficial effect by inhibition of yellowing, while the agents' water solubility could be increased by chemical modification (Hu 2003; Yuan *et al.* 2003). The effectiveness of ultraviolet absorbers and radical scavengers treatment on brightness and brightness stabilization of *Populus* alkaline peroxide mechanical pulp (APMP) was investigated by Pu *et al.* (2001) and Zhao *et al.* (2001). The yellowing inhibition effect of fluorescent whitening agents (FWA) on HYP has also been investigated by numerous authors (Ragauskas *et al.* 2001; Bourgoing *et al.* 2001; Zhang *et al.* 2007; Shi *et al.* 2012). But the self-photo stability of the FWAs still needs to be improved (Cao *et al.* 2005). Qin *et al.* (2009) synthesized a novel hindered amine yellowing inhibitor based on N,N'-bis(2,2,6,6-tetramethyl-4-piperidinyl)-1,6-hexanediamine (HMBTAD), which was shown to be beneficial to yellowing inhibition. Beaton and Argyropoulos (2001) found that benzotriazole ultraviolet absorbers and hindered amine radical scavengers had better synergistic effect on pulp yellowing inhibition. Researchers began to synthesize the multifunctional photo-stabilizer with different functional groups in a single molecule. Compounds which had the function of ultraviolet absorbing and photo stabilizing were synthesized with 2,2,6,6-tetramethyl-piperidinol and benzophenone/benzotriazole by Bojinov *et al.* (2010). Hu *et al.* (2004, 2005) designed and synthesized different kinds of yellowing inhibitors with 4-amino-2,2,6,6-tetramethylpiperidinyloxy (4-amino-TEMPO) as hindered functional groups.



**Fig. 1.** Schematic description of the light-induced yellowing process and proposed yellowing inhibition method for HYP

Coumarin and its derivatives have been applied widely as fluorescent compounds, in dye lasers, in dye-sensitized solar cells, and in many other photochemical active substances (Duarte and Hillman 1990; Mishra *et al.* 2009; Liu *et al.* 2012). Such applications take advantage of its special structure of cinnamic acid lactone (Cigan *et al.* 2013). The luminescent properties of the coumarin and its derivatives depend on the appropriate substituents at the 3-, 4-, and 7- positions of the coumarin moiety (Nag and Bhattacharyya 1990; Bangar and Varandajaran 1994; Nad *et al.* 2003; Satpati *et al.* 2009; Wagner 2009; Cigan *et al.* 2012). In the present work, 7-hydroxy-4-methyl coumarin was prepared by the Pechmann method. A fluorescent compound based on 7-hydroxy-4-methyl coumarin (FCC) was prepared (Essaidi *et al.* 2013). And with the connecting segment of polyethylene glycol (PEG), a series of polymeric fluorescent compounds (PFCC) were prepared. Their structures and properties were represented by Fourier

transform-infrared spectroscopy (FT-IR),  $^1\text{H}$  nuclear magnetic resonance ( $^1\text{H}$  NMR) spectrometry, ultraviolet–visible (UV-vis) spectroscopy, fluorescence spectroscopy, and scanning electron microscopy (SEM). The application performance was tested with an ultraviolet aging apparatus.

## EXPERIMENTAL

### Materials

The main raw materials used to synthesize the FCC and PFCC were as follows: poplar CMP (taken from Yueyang Paper Ltd.), cyanuric chlorides, 4-amion-2,2,6,6-tetrametylniperidine (4-NH-TEMPO), resorcinol, ethyl acetoacetate, p-toluene sulfonic acid (PTS), polyethylene glycol (PEG), N,N-dimethylformamide (DMF), acetone and other reagents (analytical grade, without further purification).

### Methods

#### *Synthesis of the fluorescent materials*

7-hydroxy-4-methyl coumarin was prepared by using the raw materials of resorcinol and ethyl acetoacetate and toluene-p-sulfonic acid as the catalyst. FCC was synthesized by connecting the 7-hydroxy-4-methyl coumarin, the hindered amine light stabilizer 4-amion-2,2,6,6-tetrametylniperidine into the same molecule with cyanuric chloride as a bridge. And PFCCs were prepared by connecting a series of polyethylene glycol into FCC.

#### *Preparation of the hand sheets for test*

The pulp was prepared to 10% concentration (on dry pulp) with deionized water, and then 1%  $\text{H}_2\text{O}_2$ , 0.05% EDTA, and 0.5%  $\text{Na}_2\text{SiO}_3$  (on dry pulp) were added to adjust pH at 9 to 10. After maintaining in hot water (70 °C) for 90 min, the pulp was washed to neutral with water. The handsheets (100  $\text{g}\cdot\text{m}^{-2}$ ) were made with the pulp and cut into pieces (68 mm\*73 mm). The starch solution (4%) was gelatinized at 95 °C for 30min. And surface sizing material was prepared after adding the synthesized compounds into the solution. The handsheets were coated on a Mulicoater (England) with the sizing materials. The paper samples were dried in the black box at room temperature.

#### *Characterization*

FT-IR spectra analyses of samples were carried out by using Vector-22 Fourier infrared spectrophotometer (Bruker Corporation, Germany) with KBr pellets. All FT-IR spectra were recorded by absorption mode in the wave number range of 500 to 4000  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR spectra were measured on Bruker Advance III HD 400 MHz NMR spectrometer (Bruker Corporation, Germany) in  $\text{CDCl}_3$  or  $\text{D}_2\text{O}$  solution with tetramethylsilane (TMS) as the internal standard. Elemental analysis (C, H, and N) was performed with Perkin-Elmer 2400 elemental analyzer (PERKINELMER, USA). The photo properties of the compounds were tested with the samples dissolved in ethanol aqueous solution (concn.  $2.0\times 10^{-4}$   $\text{g}\cdot\text{L}^{-1}$ ). The UV-vis absorption properties analyses of the samples were determined by Jena UV-2006A spectrophotometer (Analytik Jena AG, Germany). The fluorescent spectra of the samples were carried out on a Horiba Scientific FluoroMax-4P fluorescence spectrophotometer (HORIBA Scientific, France). The morphology of handsheets was observed using a Hitachi S-4800 instrument (Hitachi, Ltd., Japan).

### Application Performance

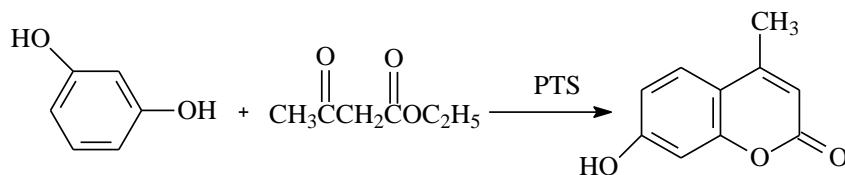
The brightness of the handsheets was determined by ZB-A colorimeter (Hangzhou Zhibang Instrument Co., China) at a wavelength of 457 nm. And the brightness numerical value was the average value of 5 times determination.

Paper anti-UV aging testing was carried out using a ZN-100N UV (Xi'an Tongsheng Instrument Manufacturing Ltd., China) light resistant climate chamber (tube of UV-340). And the test conditions were as follows: 25 °C, wavelength of the UV lamp was 340 nm, output power was 5.3 mW·cm<sup>-2</sup>, radiation for 48 h, and the distance between the samples and the lamp was 30 cm. The brightness values of the samples were determined at the set interval time.

## RESULTS AND DISCUSSION

### Synthesis of 7-Hydroxy-4-methyl Coumarin, FCC, and PFCC

The synthetic route and molecular structure of synthesis of 7-hydroxy-4-methyl coumarin are shown in Fig. 2. Resorcinol (0.1000 mol), ethyl acetoacetate (0.1000 mol), and p-toluene sulfonic acid (0.0029 mol) were added into a three-necked flask. The mixture was stirred and refluxed at 75 °C until the solution appearing light yellow. The precipitate was obtained by cooling the solution and filtering the solution. After recrystallizing in aqueous ethanol solution (60%), the target product, 7-hydroxy-4-methyl coumarin was obtained. The properties of the light yellow crystals were as follows: the yield is 94.7%; and the melting range (m.r.) is 184 to 186 °C. The element analysis results for C<sub>10</sub>H<sub>8</sub>O<sub>3</sub> (wt%): found C 68.4, H 4.51, calculated C 68.18, H 4.58.

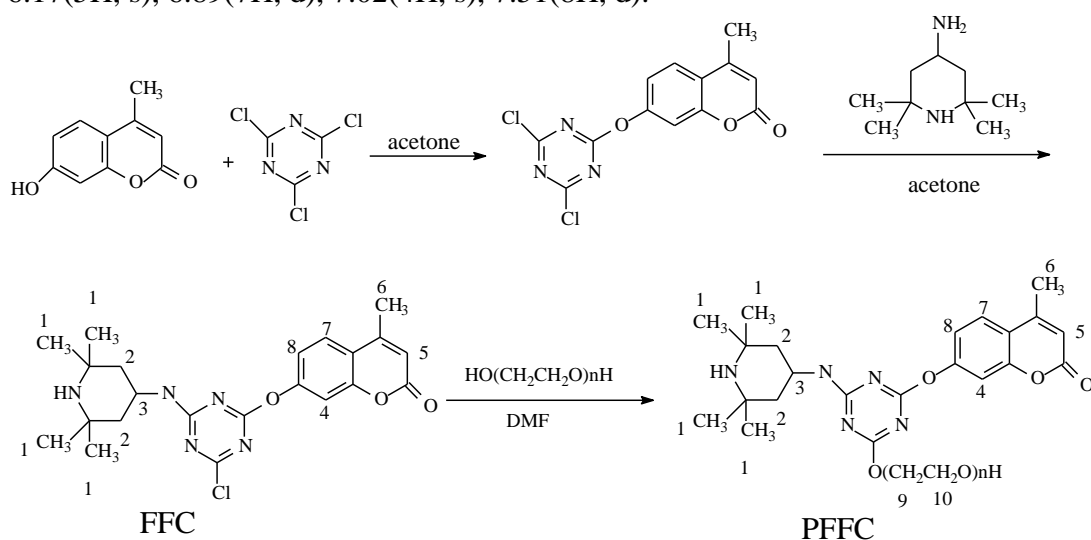


**Fig. 2.** Schematic diagram of synthetic route of 7-hydroxy-4-methyl coumarin

The synthetic route and molecular structure of FCC and PFCC are shown in Fig. 3. Cyanuric chloride (0.0249 mol) was dissolved in acetone (40 mL), and then the 7-hydroxy-4-methyl coumarin (0.0249 mol) was added into the mixture at 0 to 5 °C while 10% NaOH was used to adjust the pH to 5.5. The reaction was ended when a constant pH was achieved. 4-NH-TEMPO (0.0249 mol) was added into the mixture, then the mixture was heated to 40 to 45 °C, and the pH was adjusted to 6.5. The reaction ended when the pH remained constant. The mixture was cooled to room temperature and filtered. After collecting, washing with acetone, drying, and milling the precipitate, a yellow powder with a yield of 83.1% and melting point of 124 to 127 °C was obtained. FT-IR (KBr,  $\sigma/\text{cm}^{-1}$ ) absorbances were as follows: 3212 (-NH), 3047 (Ar-CH<sub>3</sub>), 1788 (-O-C=O), 1396, 1374, 1341 (-C-CH<sub>3</sub>), 1112 (C-O). <sup>1</sup>H NMR (D<sub>2</sub>O, 400 MHz),  $\delta$ : 1.61 (1H, m), 1.72 (4H, d), 2.25 (3H, s), 2.78 (12H, s), 6.91 (2H, d), 7.04 (2H, d), 7.31 (1H, s), 7.67 (1H, s). The elemental analysis results of FCC (wt%) were as follows: found C 59.5, H 6.03, N 15.8, calcd. C 59.66, H 5.69, N 15.81.

FCC (0.0125 mol) was dissolved in N,N-Dimethylformamide (DMF, 40 mL). PEG (overdose) was added to the solution while stirring at 95 to 98 °C, while 10 %

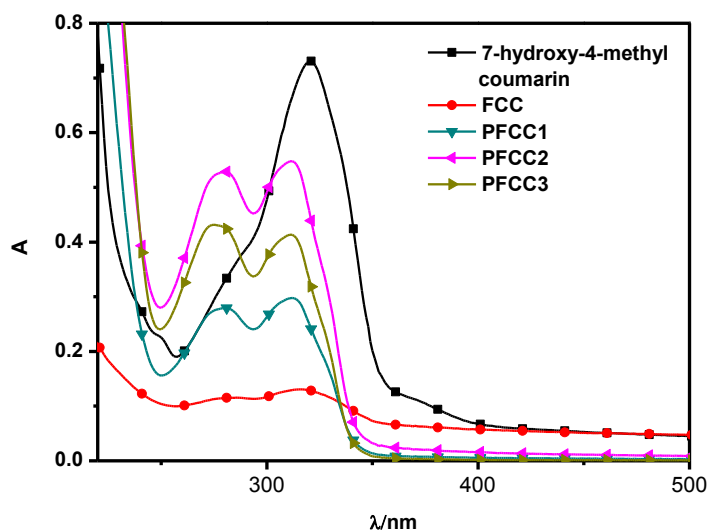
NaOH was used to adjust the pH to 7. The mixture was stirred and refluxed for about 4 h. the reaction was ended when the pH was constant. After cooling the solution to room temperature, collecting, drying, and milling the precipitate, PFCC was obtained. Different PFCCs connecting PEG-400, 600, and 800 were synthesized by the above method. When PEG-600 was used, a light yellow powder with a yield of 77.8% and m.r. 153 to 159 °C was obtained. FT-IR (KBr,  $\sigma/\text{cm}^{-1}$ ): 3447 (-NH), 1739 (-O-C=O), 1661, 1612 (C-CH<sub>2</sub>-C), 1269, 1158 (C-O); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz),  $\delta$ : 1.28(3H, t), 1.72(2H, d), 2.30(1H, m), 6.17(5H, s), 6.89(7H, d), 7.02(4H, s), 7.51(8H, d).



**Fig. 3.** Schematic diagram of synthetic route of FCC and PFCC

### Absorption Spectra

The absorption spectra of 7-hydroxy-4-methyl coumarin, FCC, and PFCC are shown in Fig. 4 (PFCC 1, 2, and 3 represent PFCC with PEG-400, 600, and 800, respectively).

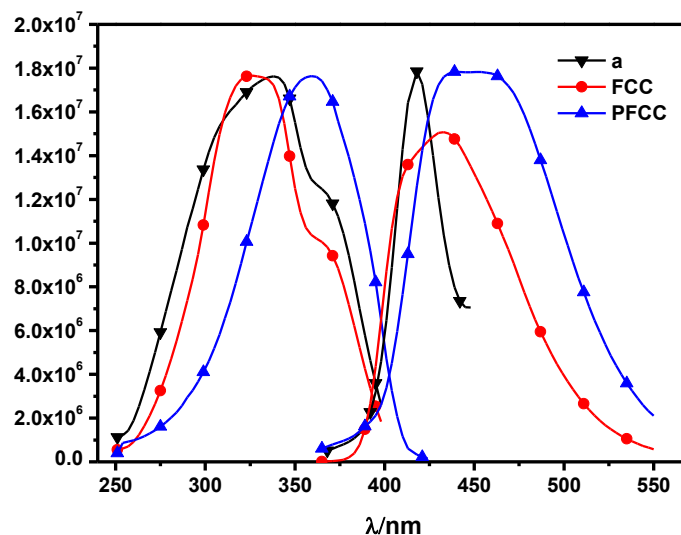


**Fig. 4.** UV spectra of the 7-hydroxy-4-methyl coumarin, FCC and PFCCs

7-hydroxy-4-methyl coumarin has one absorption peak, which is located at 321 nm. The FCC and PFCCs had two absorption peaks, which were located near 280 nm and 315 nm for the connection of 7-hydroxy-4-methyl coumarin and 4-NH-TEMPO. Different wavebands UV light could be absorbed by the two different functional groups. Compared with 7-hydroxy-4-methyl coumarin, FCC and PFCCs had wide UV-vis absorption bands and strong absorption intensity, which means FCC and PFCC had better fluorescent properties than 7-hydroxy-4-methyl coumarin. And the malposed waveband absorption of FCC and PFCC led to a more comprehensive function in absorption of near-ultraviolet light of 280 to 400 nm. The lignin will be exposed to less UV radiation due to the competitive absorption of FCC and PFCCs, which could protect lignin from UV radiation and inhibit the yellowing process of paper. FCC and PFCC show exceptional UV absorption ability, but PFCC showed better absorption effect than FCC.

### Photoluminescence Behavior

The photoluminescence spectra of 7-hydroxy-4-methyl coumarin, FCC, and PFCC (PEG-600) are shown in Fig. 5. The three kinds of fluorescent materials could absorb UV light and emit light of a purplish blue band. The results show excellent fluorescent properties. But the emission wavelength range of 7-hydroxy-4-methyl coumarin is narrower than FCC and PFCCs', which means that FCC and PFCC exhibited better fluorescent properties and whitening ability.



**Fig. 5.** Excitation and Emission spectra of 7-hydroxy-4-methyl coumarin (a), FCC and PFCC (PEG-600)

The red shift phenomenon of PFCCs' emission spectra is shown in Fig. 6. FCC and PFCC yielded blue emission within the range of 425 to 460 nm. Compared with FCC, the maximal emission peaks of PFCCs were red shifted by 20 to 30 nm (Fig. 6, PFCC 1, 2, and 3 represent PFCC with PEG-400, 600, and 800, respectively). As a kind of intramolecular conjugated compounds, the electron-releasing ability of functional groups at 7- position could affect the photo properties of coumarin and its derivatives. As an electron donor, the connecting of PEG could increase the cloud density of coumarin structure, while -Cl decreased the cloud density for its withdrawing electron ability (Donovalova *et al.* 2012).

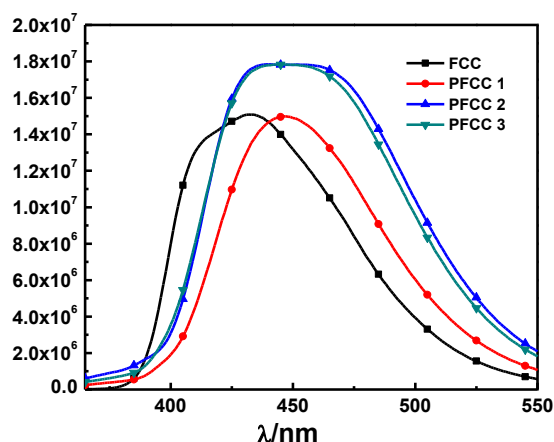


Fig. 6. Emission spectra of FCC and PFCCs

### SEM of Hand Sheets with Products

The SEM images (Fig. 7) provide a representative overview of paper with the FCC (Fig. 7 a) and PFCC (Fig. 7 b, PEG-600). The images reveal that PFCC had better water-solubility than FCC. Because of the poor water solubility, the paper with the FCC contains a large number of particles (Fig. 7 a). And the integration of FCC with fibers was also effected by the drawback. Conversely, the paper with PFCC displays smooth surface due to the presence of the PEG connecting segments, which increased PFCCs' solubility in water (Fig. 7 b).

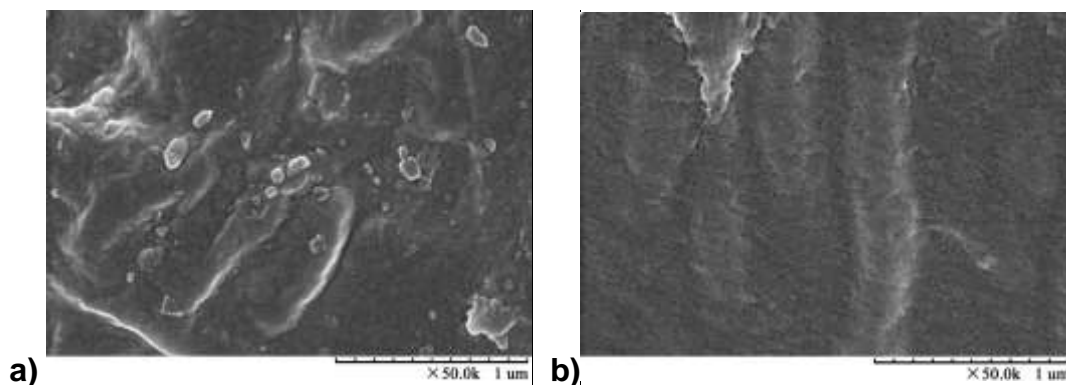


Fig. 7. SEM images of paper sheets with the FCC and PFCC

### Performance of Anti-UV Aging

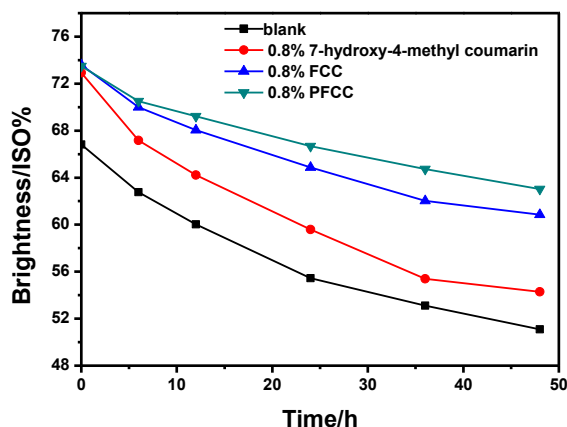
The level of anti-UV aging of paper can be represented by Post Color Number (PC for abbr.), which describes the relative quantity of the chromogenic substances when paper is under UV irradiation. A higher PC value means more chromogenic substances are contained in the paper (Zhang, *et al.* 2012). The PC value was calculated using Eqs. 1 and 2 (Chen *et al.* 1995),

$$PC = \left[ \left( \frac{k}{s} \right)_t - \left( \frac{k}{s} \right)_o \right] \times 100 \quad (1)$$

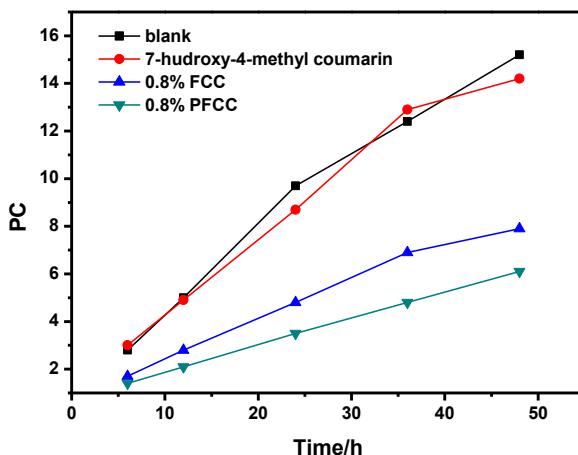
$$\frac{k}{s} = \frac{(1 - R_{\infty})^2}{2R_{\infty}} \quad (2)$$

where  $k$  and  $s$  denote the light absorption and scattering coefficients, respectively;  $R_{\infty}$  represents the brightness measured at 457 nm ( $R_{457}$ ); and the subscripts  $o$  and  $t$  denote the initial and final UV aging, respectively.

The results of anti-UV aging of paper samples are reported in Figs. 8 and 9. The coating weight of FCC and PFCC was  $0.4 \text{ g}\cdot\text{m}^{-2}$ , while the dosage of the products was 0.8%.



**Fig. 8.** Effect of different light irradiation times on the brightness of paper with coumarin, FCC, and PFCC



**Fig. 9.** Effect of different light irradiation times on the PC value of paper with coumarin, FCC, and PFCC

The initial brightness of the blank paper, paper with coumarin, FCC, and PFCC were 66.82 ISO%, 72.93 ISO%, 73.6 ISO%, and 73.49 ISO%, respectively. And after UV aging for 48 h, the brightness values were 51.09 ISO%, 54.28 ISO%, 60.85 ISO%, and 63.03 ISO%, respectively (Fig. 8). Compared with the initial brightness, the brightness of the sheets after UV aging for 48 h had decreased by 15.73 ISO%, 18.65 ISO%, 12.75 ISO%, and 10.46 ISO%, respectively. The PC values (after UV aging for 48 h) of the



blank paper, paper with coumarin, FCC, and PFCC are successively 15.2, 14.2, 7.9, and 6.1, respectively.

The increasing of paper's brightness mainly depended on the coumarin. So, paper with 7-hydroxy-4-methyl coumarin, FCC, and PFCC had the same level of brightness. But paper with FCC and PFCC showed a greater effect on anti-UV aging than coumarin. According to the yellowing mechanism, the formation of free radicals is the key step of HYP light-induced yellowing. 4-NH-TEMPO structure in FCC and PFCC could capture the radicals produced by the macromolecular compounds in a photolysis process. Coumarin structure could increase the initial brightness, and it also could absorb the UV radiation and decrease the oxidation of the lignin. The cooperation of the two functional groups brings excellent application performance to FCC and PFCC. The different anti-UV aging effect between FCC and PFCC may be due to a difference of the water solubility.

## CONCLUSIONS

1. FCC and PFCCs were synthesized, and their luminescent behavior was investigated through UV and fluorescent spectra. These fluorescent materials exhibited excellent luminescent properties. The emission spectrum of PFCC were red shifted by 20 to 30 nm for the compounds connected with PEG instead of -Cl.
2. The application performances of the 7-hydroxy-4-methyl coumarin and synthesized compounds were tested. And the results showed that these materials had beneficial effects on the increase of the paper's initial brightness and on yellowing inhibition. But the synthesized compounds had better application performances than 7-hydroxy-4-methyl coumarin. It was caused by the cooperation of the two different functional groups which could absorb the UV radiation, decrease the oxidation of the lignin, and scavenge the free radicals produced at the photolysis stage at the same time.

## ACKNOWLEDGMENTS

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