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Synthesis of polymeric fluorescent brightener based on coumarin and its performances on paper as light stabilizer, fluorescent brightener and surface sizing agent

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ABSTRACT

In this work, a novel polymeric fluorescent brightener based on coumarin (PFBC) was synthesized, using three-step synthetic route, from 7-amino-4-methylcoumarin, coumarin monomer (FBC), Acrylamide (AM) and methacrylatoethyl trimethyl ammonium chloride (DMC). The structure of PFBC was characterized by FT-IR, ^{1}HNMR and GPC. PFBC was applied to paper fiber as light stabilizer, fluorescent brightener and surface sizing agent and its performances were evaluated by measuring the UV–vis, fluorescence, thermal stability, the cationic degree, surface strength and smoothness of paper, the brightness degree of paper and the PC value of paper. Results showed that PFBC had better solubility in water than that of FBC, by measuring the optical properties. Through the surface sizing experiment and UV aging experiment, PFBC not only enhanced the surface strength and smoothness of paper as a surface sizing agent, but also had better effect on anti-UV aging than that of FBC as light stabilizer and fluorescent brightener.

1. Introduction

With the limit of forest resources all over the world, high-yield pulp (HYP) has been gaining increasing interests in the manufacturing of uncoated and coated fine paper and paperboards, for its attractive features: high bulk, high opacity, high stiffness and good printability. However, one of main drawbacks of HYP is the color reversion since it contains much more lignin [1–4]. The special chemical structure of lignin is easily influenced by certain external environment, such as, temperature, light and the presence of metal cations. Among them, the light is the main factor. When the lignin is long term exposed under the sunshine, its structure can easily generate chromophores or auxochromes, losing the brightness of paper to make it yellowing. It leads to the weakness of light stability, especially brightness stability of HYP, which greatly hindered its application in some high-value paper. According to the research about light-induced yellowing mechanism of HYP, different proposed yellowing inhibition methods were studied, such as, chemical modification of lignin, exploring new bleaching process of high yield pulp and adding chemical auxiliaries. From the perspective of cost and effect of light stability, adding chemical auxiliaries (ultraviolet absorbents, radical scavenger and fluorescent brighteners, et al.) is considered as the most feasible method to exhibit the yellowing of HYP.

The fluorescent brightener agents could be primarily applied to paper to enhance their whiteness and brightness characteristics because it increases the UV-blocking properties by absorbing light in the near ultraviolet region and re-emitting at a longer wavelength in the blue and visible region [5–10]. The coumarin and its derivatives as important classes of FBAs have been widely used in the paper making field for its high fluorescence quantum yield and good light stability [11–18]. However, there still exist some deficiencies. As is well known, coumarin and its derivatives are all small organic molecules with little hydrophilic groups in their structures, resulting in poor water-solubility, bad combination with the paper fiber and uneven dispersion on the surface of paper fiber. They need to be dissolved in the organic solvents with large dosage when coated on the surface of paper, which not only has negative effect on their whitening and yellowing inhibition properties, but also on human health and the environment. In addition, the solutions of coumarin and its derivatives have no adhesive property and film-forming property. Therefore the practical applications of coumarin and its derivatives are limited. In order to overcome the shortcomings mentioned above, the synthesis of water-soluble, cationic or polymeric fluorescent brightener agent has become an intriguing topic [19–24].

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Herein, to endow coumarin and its derivatives with useful properties, a novel polymeric fluorescent brightener based on coumarin (PFBC) was synthesized by copolymerization, containing DMC, AM and FBC. As a cationic monomer, DMC can provide improvements in adhesion on the surface of paper on account of its positive charge and high polarity and AM plays an important role in the copolymerization as a bridge. The novel synthetic method for the preparation of PFBC makes the water-insoluble coumarin fluorescent monomer turn into a multifunction polymer with water-soluble and adhesive property. Results showed that PFBC not only has higher hydrophilicity, light stability and brightness than those of FBC as light stabilizer, and fluorescent brightener, but also enhances the surface strength and smoothness of paper as surface sizing agent.

2. Materials and methods

2.1. Materials and equipment

The main raw materials used to synthesize the 7-amino-4-methylcoumarin, FBC and PFBC were as follows: 3-aminophenol (Sinopharm Chemical Reagent Co. Ltd, Shanghai, China), ethyl acetoacetate, zinc chloride ($ZnCl_2$), anhydrous ethanol (CH_3CH_2OH), concentrated sulfuric acid (H_2SO_4), isopropanol ($(CH_3)_2CHOH$), trichloromethane ($CHCl_3$), triethylamine ($N(CH_2CH_3)_3$), Acryloylchloride (C_3H_3ClO), ammoniumpersulfate ($(NH_4)_2S_2O_8$), urea ($CO(NH_2)_2$), methacrylatoethyl trimethyl ammonium chloride (DMC), Acrylamide (AM) (analytical grade, Tianli Chemical Reagent Co. Ltd, Tianjin, China), poplar chemi-mechanical pulp (CMP, Yueyang Paper Ltd., China). FT-IR spectra analyses were recorded on the VECTOR-22 FT-IR spectrometer (Bruker Corporation, Germany) with KBr pellets. ^{1}HNMR spectra was measured on Bruker Advance III HD 400 MHz NMR spectrometer (Bruker Corporation, Germany) in $DCCl_3$ and DMSO solution with tetramethylsilane (TMS) as the internal standard. UV spectra were measured using the Cary 100UV–Visible Spectrophotometer (Agilent, USA). Fluorescence spectra were measured on a Fluorolog spectrofluorometer (HORIBA, France). The TGA curve recorded on the TGA Q500 (TA, USA). Zeta potential was recorded in the Zetasizer NANO-ZS90 (Malvern, UK). The brightness was recorded on ZB-A colorimeter (Hangzhou Zhibang Instrument Co. Ltd, China). The morphology of handsheets was observed by the S4800 SEM images (Rigaku, Japan).

2.2. Synthesis

2.2.1. Synthesis of 7-amino-4-methylcoumarin

Based on the Pechmann method [25], 7-amino-4-methylcoumarin was synthesized by using 3-amino phenol and ethyl acetoacetate, catalyzed by zinc chloride. The synthetic route was showed in Fig. 1. Typically, 9.7 g of 3-amino phenol, 5.45 g of ethyl acetoacetate, 8.5 g of zinc chloride and 30 mL of anhydrous ethanol were added into a 100 mL round-bottom flask, equipped with a stirring bar, thermometer and a reflux condenser. Under the protection of nitrogen, the mixture was then stirred for 14 h and the temperature was maintained at 90 °C. The progress of reaction was monitored by thin layer chromatography (TLC). At the end of the reaction, the product was isolated by adding 200 mL of 0.1 mol L^{-1} HCl solution. Then the product was precipitated out and filtered by vacuum pump, and the precipitate was washed with distilled water two times to remove the unreacted reactants and catalyst. The product was dried in vacuum drying oven overnight at room temperature. Finally, the dried product was recrystallized by isopropanol. The purified product was dried under vacuum overnight at 40 °C and stored in a desiccator. The yield: 40.5%. ^{1}HNMR: (400 MHz, $DCCl_3$, 40 °C): d/ppm: 2.38 (s, 3H, CH_3), 4.17 (s, 2H, NH_2), 6.05 (s, 1H, corresponding to proton of double bond in the vicinal of methyl), 6.57 (s, 1H, ArH), 6.59 (d, 1H, ArH), 7.38 (d, 1H, Ar). I.R. (KBr):3440 cm^{-1}, 3353 cm^{-1} (NH_2 Stretch); 2981 cm^{-1} (CH3 Stretch); 1692 cm^{-1} (O=C Stretch); 1618 cm^{-1}, 1539 cm^{-1}, 1449 cm^{-1}, 1396 cm^{-1} (Ar Stretch); 1263 cm^{-1}, 1216 cm^{-1} (C-O-C Stretch).

2.2.2. Synthesis of FBC

To a 250 mL round-bottom flask with a stirring bar, thermometer, a reflux condenser and nitrogen protection, 5 g of 7-amino-4-methylcoumarin, 50 mL of trichloromethane and 8.7 g of triethylamine were added. To this stirred mixture, 3.1 g of a solution of acryloyl chloride in 30 mL of trichloromethane was added dropwise maintaining temperature at-5-0 °C. After dropping, the reaction liquid was heated to 60 °C and stirred for 6 h. FBC was isolated by vacuum pump and the precipitate was washed with distilled water two times. Then the product was dried in vacuum drying oven overnight at room temperature. The synthetic route was showed in Fig. 2. The yield: 39.6%. ^{1}HNMR: (400 MHz, DMSO, 40 °C): d/ppm: 2.51 (s, 3H, CH_3), 5.83 (d, 1H, CH=), 6.31 (q, 2H, CH_2=), 6.51 (s, 1H, ArH), 7.56 (d, 1H, ArH), 7.76 (d, 1H, ArH), 7.87 (s, 1H, corresponding to proton of double bond in the vicinal of methyl), 10.62 (s 1H, NH). I.R. (KBr):3313 cm^{-1} (NH Stretch); 3113 cm^{-1}, 3089(C=CH Stretch); 1793 cm^{-1} (O=C Stretch), 1684 cm^{-1} (O=C-NH Stretch), 1618 cm^{-1} (C=C Stretch), 1528 cm^{-1}, 1502 cm^{-1}, 1455 cm^{-1}, (Ar Stretch); 1409 cm^{-1} (C-N Stretch); 1268 cm^{-1}, 1223 cm^{-1} (C-O-C Stretch).

2.2.3. Synthesis of PFBC

The synthetic route of fluorescent polymer was showed in Fig. 3. Under the oxidation-reduction system ($(NH_4)_2S_2O_8$ – $CO(NH_2)_2$, $W_{(NH_4)_2S_2O_8}$: $W_{CO(NH_2)_2}$ = 1 : 1), the FBC, AM and DMC (the molar ratio: n_{FBC}:n_{AM}:n_{DMC} = 1:4:5) with a mixture of ethanol and water solution as solvent were gradually added to a 250 mL round-bottom flask with a stirring bar, thermometer and nitrogen protection. The mixture was stirred for 6 h maintaining temperature at 30 °C. At the end of the reaction, PFBC was isolated by vacuum and the solution was evaporated by the Rotary evaporator. Then the product was recrystallized with trichloromethane and distilled water to remove the unreacted monomers and dried in vacuum drying oven overnight at 80 °C. The synthetic route was showed in Fig. 3. The yield: 41.2%. ^{1}HNMR: (400 MHz, DMSO, 40 °C): d/ppm: 1.04–2.41 (CH-CH2, CH3 of the main chain), 2.48 (s, 3H, CH3 of coumarin), 2.95–3.45 (CH3 of DMC), 5.58 (s, NH2 of AM), 6.89 (ArH), 7.56 (ArH), 7.29 (ArH), 7.11 (ArH). I.R. (KBr):3413 cm^{-1} (NH Stretch); 2964 cm^{-1} (CH2 Stretch); 1721 $cm^{-1}$and 1669 cm^{-1} (O=C Stretch); 1585 cm^{-1}, 1529 cm^{-1} and 1479 cm^{-1} (Ar Stretch); 1481 cm^{-1} (CH2-N(CH3)3 deformation); 1268 cm^{-1} and 1228 cm^{-1} (C-O-C Stretch).

2.3. Preparation of the hand sheets for test

With the deionized water, the pulp was prepared to 10% concentration (on dry pulp), and then 1% H_2O_2, 0.05% EDTA, and 0.5% $Na_2SiO_3{\cdot}9H_2O$ (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 deionized water. The hand sheets (100 g m^{-2}) were made with the pulp and cut into pieces (68mm × 73 mm). And surface sizing material was prepared after adding the synthesized compounds into the solution. The hand sheets were coated on the coating machine (ST-1-260, Shaanxi University of Science & Technology, China) with the sizing materials. In the opaque background, the paper samples were dried at room temperature [11].