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Producing fluorescent digital printing ink: Investigating the effect of type and amount of coumarin derivative dyes on the quality of ink

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ABSTRACT

The aim of this work is to produce a composite powder as a fluorescent ink for digital electrophotographic printing. Three benzoxazolyl and benzimidazolyl coumarin derivative dyes are used as fluorescent dyes that are incorporated into poly (styrene-co-a crylic acid) using eco-friendly emulsion aggregation (EA) approaches in several amounts with final application of fluorescent laser printing ink called toner. Fluorescence and daylight spectrophotometry is used for investigating the emission and reflectance properties of fluorescent toner. It was found that the relations between emission of fluorescent toners and the amount of dyes are non-linear. Particle size analysis, scanning electron microscopy, differential scanning calorimeter and thermal gravimetric analysis were used to study the size, shape, morphology and thermal properties of fluorescent toner particles. Results verify that the polarity of the dyes and their compatibility with the environment could affect the shape of the fluorescent toner. In addition, the results show that the fluorescent toner produced by the EA method has appropriate characteristics comparing to an industrial toner.

1. Introduction

Daylight fluorescent colorants were first launched in the middle of 20th century for applications requiring high visibility such as road markers, safety jackets, warning devices, highlighting markers, toys [1] and optical brighteners [2]. Fluorescent molecules absorb in the ultraviolet wavelength range (320–380 nm) and emit light in part of the visible wavelength range (380–730 nm) [3]. This feature of fluorescent molecules makes them suitable to be used as functional dyes. Nowadays, fluorescent colorants are widely used for preparing inks [4–9]. In 2004, Coyle and Smith [10] described the use of red, green and blue emitting fluorescent inks for creating color images with an inkjet printer in 2014; Talebtina et al. [11] introduced the yellow fluorescent inks for lithographic printing ink. Letterpress, lithographic, gravure, flexographic, and screen are some of the common conventional printing methods and ink jet and electrophotographic are some of the favorite digital printing methods [8,9].

Among the mentioned digital printing methods, electrophotographic method, which is used in copy machine and laser printer, has attracted interest in recent years as one of the major technologies for document printing, serving a wide range of market applications [12]. The electrophotographic printing ink, which is called toner, is a composite of polymer, colorant and other additives that are essential for the printing process [13]. The possibility of introducing a new kind of toner for document printing market associated with the promotion of common toner properties is a beneficial feature from industrial and academicals point of view, which lead us to produce fluorescent toner. In the series of previous studies, the authors studied the production of black [14] and color [15] toner with eco-friendly emulsion aggregation (EA) and polymerization [16] method. It was shown that high rotating speeds are frequently required to obtain uniformly-sized small particles. We also illustrated that pigments with higher polarity are liable for better compatibility and dispersion, where toners with smaller particle size and particle size distribution were yielded. Besides the authors studied the synthesis [17] and application [11] of coumarin derivative dyes. Coumarin derivatives afford a range of organic materials that are used commercially in a broad range of applications because of their intense fluorescence. As significant organic fluorescent chromophores are widely used in the synthesis of laser dyes, fluorescent whiteners, organic nonlinear optical materials, and coloring of textiles and other

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materials. They find considerable importance in industry and academic use [17].

In continuation of our works, for the first time, the current study introduces the fluorescent toner for electrophotographic printing, which raises a number of challenges. One of the most common challenges of using fluorescent colorants in ink is the effect of formulation on fluorescence properties of dyes and also the optimum amount of fluorescent dyes in formulation to obtain maximum emission. At low concentrations of fluorescent molecules, the fluorescence phenomenon shows a linear relationship with the concentration, but at high concentrations, the linear relationship disappears. This non-linear phenomenon is known as quenching [18,19]. Herein, benzoxazolyl and benzimidazolyl coumarin derivatives dyes as 3-(5-Chloro-2-benzoxazolyl)-7-(diethylamino)-2H-1-benzopyran-2-one, **1a**, 3-(5-Methyl-2-benzoxazolyl)-7-(diethylamino)-2H-1-benzopyran-2-one, **1b**, and 3-(2-Benzimidazolyl)-7-(diethylamino)-2H-1-benzopyran-2-one, **1c,** with different concentrations were used to prepare monodisperse semi-spherical composite with poly (styrene-co-acrylic acid) by using an eco-friendly method named emulsion aggregation (EA), which for the first time, can be used as the daylight fluorescent electrophotographic printing toner. Moreover, the quenching of emissions owing to media and concentration of fluorescent dye was studied.

2. Experimental

2.1. Materials

The polymer used in this study was a styrene-acrylic resin (R579; ResinFam Co., Iran) with a pH value of around 9 and T_g (glass transition temperature) of 51 °C, and mean particle size of 220 nm, according to the supplier. A polyethylene emulsion wax was purchased from Kala Kar (EE 95, Kala Kar Co., Iran). Poly-aluminum chloride from Merck Company was used as a coagulating agent. All the mentioned materials were used as received.

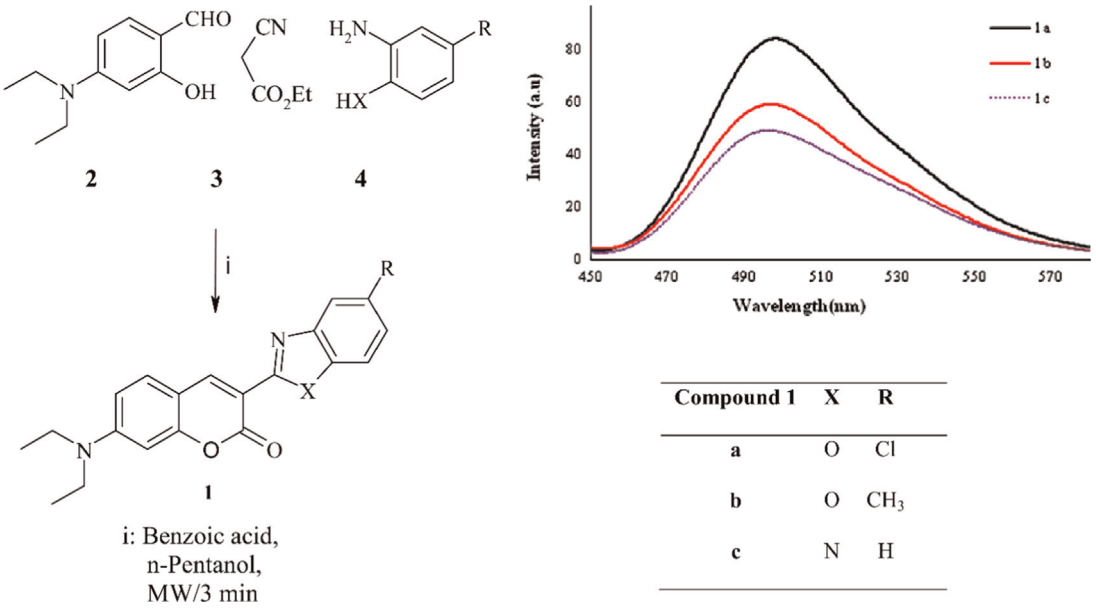
Three coumarin based fluorescent dyes as shown in Fig. 1 were produced by a microwave-assisted one-pot procedure according to our previous studies [17]. The purity of the produced dyes (more than 90%) was monitored by TLC. All the dyes **1** (a–c) were excited at 435–436 nm and showed green fluorescence emission with high intensity (λ_{max} at 490–500 nm). Fig. 1 shows fluorescence emission spectra of 10^{-7} M acetonitrile solutions of the three dyes [11].

2.2. Preparation of fluorescent printing toner

In this study, all the toners were prepared using the same procedure in accord with the authors' previous studies [14,15,20,21]. This procedure included eight steps. In step *a*, a one-liter beaker was filled with 24.5 g styrene-acrylic latex (particle size: 220 nm), various amounts of each fluorescent dye, 3 g wax and 120 g deionized water. Then, the contents were mixed manually at room temperature for 15 min. In step *b*, the contents were mixed by a homogenizer for 5 min at the agitation speed of 5000 RPM. In step *c*, the mixture was continuously mixed for 60 min at room temperature and a solution of 0.6 g coagulation agent in nitric acid was added drop-wise over 10 min until the pH value of the mixture reached 2. During this process, a gel was formed that changed the viscosity of the suspension from a Newtonian water-like fluid to a shear thinning paste-like gel. In step *d*, temperature of the mixture was increased to 50 °C for about 60 min while the gel was continuously mixed. In step *e*, the mixture was held at this temperature for another 60 min. In step *f*, the temperature of the mixture was increased to 96 °C for 60 min, and in step *g*, it was held at this temperature for a further 60 min. The mixture was neutralized with sodium hydroxide solution after temperature increased. Finally, the mixture was cooled to 25 °C, after which the produced micro-particles were isolated from the water, washed to remove divalent ions, filtered, and dried with a frizzed dryer. All the mixing was done at the agitation speed of 1200 RPM. Fig. 2 shows the variation of pH and temperature over the course of the toner synthesis process and the scheme of the preparation [14].

Based on mentioned procedure, the several sets of experiments were performed with different type of fluorescent dyes. Various concentrations were used for each fluorescent dye, namely, 0.25%, 0.5%, 0.75% and 1% by weight of the toner. Such fluorescent toners were then named as $Ta_{0.25}$, $Ta_{0.5}$, $Ta_{0.75}$ and Ta_1 for fluorescent dyes with component **1a**, $Tb_{0.25}$, $Tb_{0.5}$, $Tb_{0.75}$, and Tb_1 for fluorescent dyes with component **1b**, and finally, $Tc_{0.25}$, $Tc_{0.5}$, $Tc_{0.75}$ and Tc_1 for fluorescent dyes with component **1c**. For fluorescent toners prepared with fluorescent dyes with component **1c** an extra dye concentration of 1.5% is applied and named as $Tc_{1.5}$ due to complete emission behavior of the toner.

The resultant antibacterial toner nanocomposites were printed on a paper without optical brighteners in a controlled



Compound 1	X	R
a	O	Cl
b	O	CH_3
c	N	H

Fig. 1. Synthesis of the coumarin derivatives 1(a–c) and their emission spectra (10^{-7} M in acetonitrile solutions) using 1% filter [11,17].