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minPreparation and characterization of organic pigments and their fluorescence properties depending on bulk structure

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ABSTRACT

Fluorescent pigments, based on the optical or electrooptical properties of dyes, are the main component in fluorescent coatings and inks. In this study, three kinds of dyes (Rhodamine B, Light Green SF Yellowish, Coumarin) with four different ratios (2.5 wt%, 3 wt%, 3.5 wt%, 4 wt%) were employed as luminophor, and the melamine-formaldehyde (MF) resin was used as curing resin to prepare fluorescent pigments in different color. Fourier transform infrared spectroscopy and X-ray diffractometry were carried out to analyze the structure of the fluorescent pigments. Scanning electron microscopy and particle size distribution were used to present the morphology of fluorescent pigments. UV–vis and fluorescence spectrum were used to demonstrate the optical properties. It can be concluded that, coumarin pigments possessed consecutive structure in MF resin while rhodamine B might be the best for the preparation of printing inks among the three kinds of dyes from the view of particle size. The TG results presented that all the pigments showed good thermal stability, which might possess potential application in high speed printing industry.

1. Introduction

It is well known that dyes exhibit diverse optical or electrooptical properties with potential applications in printing industries [1], photorefractive applications [2], non-linear optical devices [3], and anti-counterfeiting techniques [4]. Fluorescent pigments, based on the optical or electrooptical properties of dyes, can absorb visible and ultraviolet light to transform the unfeeling UV fluorescence into a certain color of visible light due to the higher intensity of reflected light than ordinary colored material [5]. In this way, pigments may emit very bright colors within the visible wavelength range. Fluorescent pigments are widely used in many industries, such as commercial decoration, advertising, safety sign, children's toys, packaging, textile, plastic coloring, paint, ink, printing and dyeing [1,6]. The pigments with excellent optical properties have potential applications ranging from commodity packaging to commercial decoration.

The preparation of fluorescent pigments has generally received considerable attention in recent twenty years. The initial fluorescent pigment is refined and composed of barium, strontium, barium or zinc sulfide, a small amount of sodium chloride as flux and copper chloride as trace activator. Recently, most researchers focused on the preparation of metal-based fluorescent pigments, such as Al [7], rare-earth metals [8–11], Mo [12] and other nano-materials [13] and so on. Among them, several researchers have paid attention to the synthesis processes in preparing fluorescent pigments. Wang et al. [14] prepared a novel fluorescent pigments mixture by combination of fluorescein and tetraethoxysilane. With the catalysis function of acetic acid, tetraethoxysilane could be hydrolyzed, forming mesopore to absorb fluorescein to form homogenous luminous compound. Wu et al. [15] employed rhodamine B as luminous component, which was supported on the acid activated sepiolite (AAS/Rhb) to prepare organic/inorganic compound to form fluorescent pigments. The novel fluorescent iminocoumarins synthesized by using an efficient microwave method which has some features of short-reaction time, moderate yields and simple

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workup [16,17]. Besides, some researchers paid attention to polymeric and biological fluorescent dyes. A new strategy to prepare novel polycondensable fluorescent dyes by condensation reaction of 3-(2-benzimidazolyl)-7-(diethylamino)-coumarin (8GFF) and pyromellitic dianhydride and then reacting polyethylene glycol (PEG) with the condensate intermediate [18]. Fakhfakh et al. [19] synthesized new iminocoumarin dyes bearing a cyano group at the 3-position and a diethylamino group at the 7-position. The water-soluble and yellow-green fluorescent pigments were produced by pseudomonads [20,21]. There are also other methods for fabricating fluorescent pigment by combining red organic fluorescent pigment with the $SrAl_2O_4$: Eu^{2+}, Dy^{3+} particles [22]. In these experiments, the synthesis steps of fluorescent pigments are complex and difficult to control and operate, or the employed raw materials are rare earth elements which may limit mass production in industries. In this work, organic fluorescent pigments were prepared by using different polymers instead of rare earth materials. It is known that bulk fluorescent pigments are mainly prepared via the way that fluorescent dyes are dispersed in a transparent resin, such as Melamine-formaldehyde (MF) resin. Firstly, fluorescent dyes are mixed with resin dispersion to form solid bulk structure. And then, crisply and easily crushed products can be obtained with good thermal stability and solvent resistance with high degree of cross-linking resin. This process, namely the bulk resin pulverization method, is a popular method for the preparation of fluorescent pigments. It is easy to operate, simple in process and capable of obtaining high-density and high-gloss fluorescent pigments [23]. Therefore, it is still the most widely used method. In preparing the pigments, melamine-formaldehyde (MF) is a kind of resin which can meet the function as the fluorescent dye carrier block resin. MF resin can give the fluorescent pigment good thermal resistance and uniform pigment particle size. Notably, the MF resin is transparent, which may not cover the color of dyes. In this way, the fluorescent pigments in sunlight are solid mixture of transparent resin and dyes. In comparison, the bulk resin pulverization method is much easier to operate and capable of obtaining fine fluorescent pigments.

Because of the optical properties of dyes, fluorescent pigments can emit very bright colors within the visible wavelength range and the pigments can be used in many industries. The pigments with optical properties have been widely studied [14,17–19,22]. However, it should be emphasized that in these studies, most researches only proved that the pigments synthesized in novel way have optical properties, and few works explored the relation between concentration of dyes of different color and optical properties of fluorescent pigments. For example, Elgemeie et al. [17] only studied the optical properties of obtained dyes under microwave irradiation. Fakhfakh et al. [19] found that the optical properties of dyes strongly depended on the nature of the substituent borne. Wang et al. [14] investigated the effect of tetraethoxysilane (TEOS) concentration on the thermal- and photo-stability properties of the hybrid fluorescent pigment. Zhu et al. [22] investigated the content of red organic fluorescent pigment concentration on the optical properties of the red organic fluorescent pigment-doped hybrid

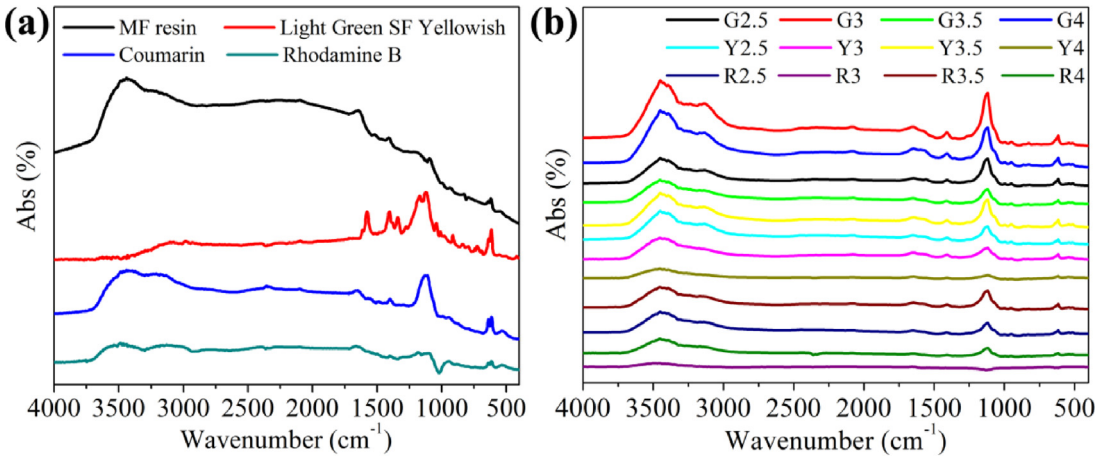

Fig. 1. FTIR spectra of samples: (a) MF resin and three dyes, (b) fluorescence pigments samples synthesized from three different dyes with different ratio.

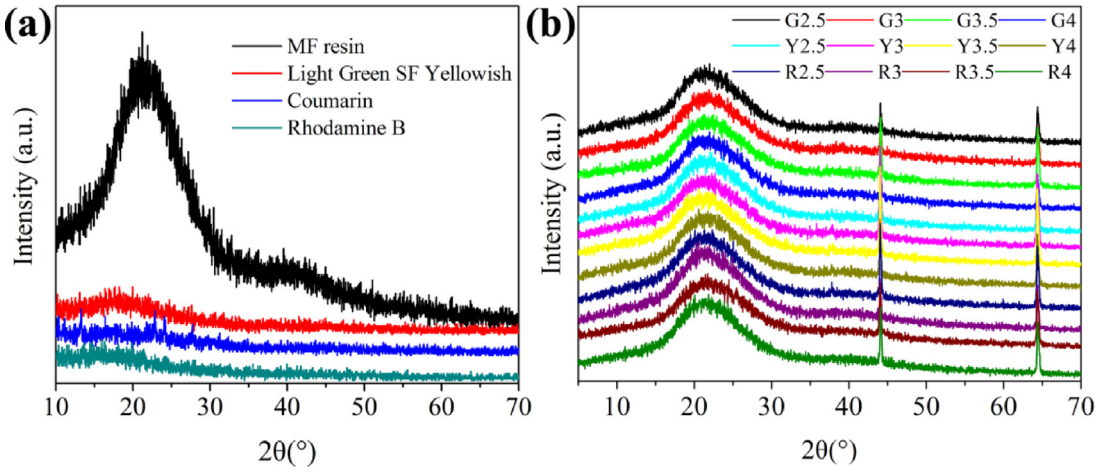

Fig. 2. XRD curves of samples: (a) MF resin and three dyes, (b) fluorescence pigments samples synthesized from three different dyes with different ratio.

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