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# Preparation of color polymeric nanomaterials containing dispersed dye by sunflower oil synergy and color transfer property by digital inkjet printing

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ABSTRACT

The color polymeric nanomaterials containing highly dispersed dye molecules were designed and prepared by sunflower oil synergy microemulsion polymerization. The color nanoparticles can be applied to coat on the PET fabrics by digital inkjet printing technique. The sunflower oil as a dye solubilization and polymer plasticizer was used in the polymerization process. The structure and morphology of polymeric nanoparticles containing dispersive dyes were characterized by Fourier transform infrared spectrum (FT-IR), field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM) and X-ray powder diffraction (XRD) analysis. The color transfer properties from nanoparticle coating into PET fabrics by digital inkjet printing were discussed. Three color nanoparticles were homogeneous nanospheres with regular shape and size below 100 nm. The nanoballs were swelled by sunflower oil. The dye is evenly dispersed in colloidal nanoparticles. The color transfer rate of three nanoparticles containing disperse dyes with 2.43% oil by digital inkjet printing method were 97.1%, 95.3%, and 96.1%, respectively. The color transfer rates of three color nanomaterials with sunflower oil were obviously improved. The fastness properties of the PET fabrics printed with three nanoparticles with oil were excellent.

## 1. Introduction

Digital inkjet printing and 3D printing as advanced coating techniques have received wide attention in many fields because of computer control and its image and shape fidelity [1–4]. The digital inkjet printing offers simplicity, high speed, pattern creativity, high image quality, cleaner production and eco-friendly [5–7]. Digital inkjet printing works in the way that drop-on-demand coating method produces patterns by the nozzle computer controlled. The design and preparation of printing coating materials have aroused wide interest [8,9]. Ink materials for textile fabric printing are usually dye-based or pigment-based inks. The pigment and binder are the necessary main ingredients in the pigment ink formulations. The dye-based inks including reactive dyes and disperse dyes are applied to print cellulose fabrics and polyester fabrics (PET), respectively.

In recent years, nanomaterials and nano-doped technique has become a research hotspot in the advanced coating materials [10–13]. The milling method of coating materials or ink materials represents one of the most popular approaches to produce the required powder particles. Due to the high surface energy of the nanoparticles, they tend to aggregate into bigger particles [14,15]. The bigger particles can block the fine nozzles of an inkjet print head and affect printing properties. It is important to investigate the preparation nano-sized ink particles to prevent the agglomeration of the nanoparticles and blocking the fine nozzles of an inkjet print head [16,17]. The encapsulation of the particles with a coating polymer layer is an alternative way. Several methods have been reported for the encapsulation of pigment particles, such as dispersion, emulsion, and microemulsion polymerization [18–20]. However, the encapsulation of particles for disperse dyes can affect dye molecule transferring from coating films into fabrics, which can further affect the color yields of the printing fabrics. To obtain stable nanoparticles, some new printing or coating materials have been developed [21–23]. Sunflower oil is a kind of natural cooking oils. It has certain solubility for dispersive dye, and can stabilize and plasticize to the polymer microemulsion particles.

In this paper, new color polymeric nanomaterials with highly dispersed dye molecules were prepared by sunflower oil synergy microemulsion polymerization. Three dispersive dyes were used to prepare color nanoparticles. The structure and morphology of color polymeric nanoparticles containing dispersive dyes were characterized by TEM, XRD and FESEM. The color transfer properties from coating nanofilms into PET fabrics by digital printing were discussed.

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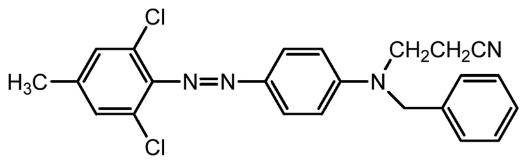
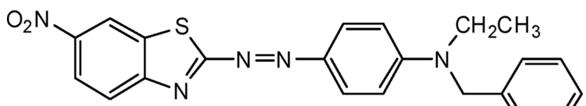
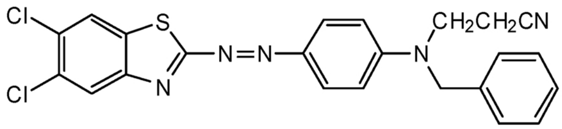


Yellow BROB



Blue 825



Red 902

**Scheme 1.** Chemical structures of three disperse dyes.

## 2. Experimental

### 2.1. Materials

Sunflower oil was purchased from Shandong Yujinxiang Food Company, Laiwu, China. Methyl methacrylate (MMA) and butyl acrylate (BA) were purchased from Shanghai Chemical Reagent Plant, Shanghai, China. MMA and BA monomers were purified by distillation under the reduced pressure before use. Sodium dodecyl sulfate (SDS) and nonionic surfactant, Tween 80, were obtained from Huangma Chemical Company, Shangyu, China. Disperse Yellow BROB, Red 902, and Blue 825, were obtained from Zhejiang Wanfeng Chemical Company, Shaoxing, China. Chemical structures of three disperse dyes are shown in Scheme1.

PET fabrics (54 × 48) were obtained from Zhejiang Jinqiu Dyeing and Finishing Company, Shaoxing, China. Other chemicals were from Shanghai Chemical Reagent Plant, Shanghai, China.

### 2.2. Dissolution of the dispersive dyes and preparation of microemulsion

A certain amount of dispersive dye is dissolved in the MMA:BA mixture monomers. The dye solution is a color transparent solution. Then, sunflower oil, emulsifier SDS, and Tween 80 were added into the dye solution according to the recipe (shown in Table1). A certain amount of water was slowly dropped into the monomer solution (oil phase) at room temperature under stirring. Then, the emulsion was stirred with 4500 r/m in the emulsifying machine until a homogeneous microemulsion (the oil in water, O/W) was obtained. Three recipes of the microemulsion are shown in Table1.

**Table 1**
Recipes of the microemulsions.

| Chemicals | Weight ratio (%) | | |
|---|---|---|---|
| MMA:BA = 3:1 | 27.80 | 27.80 | 27.80 |
| Yellow BROB | 2.43 | | |
| Red 902 | | 1.74 | |
| Blue 825 | | | 1.74 |
| Sunflower oil | 0-2.43 | 0-2.43 | 0-2.43 |
| SDS | 0.53 | 0.53 | 0.53 |
| Tween-80 | 1.06 | 1.06 | 1.06 |
| Ammonium persulphate | 0.15 | 0.15 | 0.15 |
| Isopropanol | 0.50 | 0.50 | 0.50 |
| Deionized water | 65.1–67.53 | 65.79–68.22 | 65.79–68.22 |

### 2.3. Preparation of color polymeric nanomaterials

The homogeneous microemulsion obtained was transferred into four neck flack equipped with thermometer, condenser, and stirrer. When the microemulsion was heat to 80 °C under nitrogen, a certain amount of the initiator, ammonium persulphate, was slowly dropped into the microemulsion. The polymerized reaction was carried out for 4 h at 85 °C. The color polymeric nanoparticle colloid was obtained.

### 2.4. Characterization of the nanoparticles

The particle size of the color polymeric nanoparticle was determined by Laser Particle Size Analyzer, LS-13320 (Beckman Coulter, Inc., Brea, USA). Fourier Transform Infrared Spectrum (FTIR) was measured using a Nexus-670 FT-IR spectrometer (Nicolet Analytical Instruments, Madison, WI, USA).

The morphology of the nanoparticles was observed by Field Emission Scanning Electron Microscopy (FESEM) S-4800 (HITACHI, Japan). TEM data were obtained with an FEI TF20 electron microscope. The X-ray powder diffraction (XRD) pattern was obtained using a Bruker D8 Advanced Diffractometer with Cu $K_\alpha$ radiation ($\lambda$ = 1.5406 Å).

### 2.5. Color transfer properties by digital inkjet printing

Three monochrome block patterns were printed by digital inkjet printing machine Epson L301, respectively. The samples printed were dried under 90 °C, and then cured for 4 min at 180 °C. The printed samples were reduction clearing in the solution consisting of sodium hydrosulfite, 0.5 g/l, and sodium carbonate, 1.0 g/l, for 15 min at 75 °C. Then, all the samples were rinsed with water until the rinsing water was clear and dried.

The color yield ($K/S$) and colorimetric data of the printed fabrics were determined by Datacolor SP600$^+$ spectrophotometer (Datacolor Co., Lawrenceville, NJ, USA). The tristimulus values $X$, $Y$ and $Z$ of the samples were measured under illuminant $D_{65}$ using the 10°standard observer in the visible spectrum region 360–700 nm. The absorbance and the reflectance at the wavelength of maximum absorption ($\lambda_{max}$) was used to calculate the color yield of the dyed fabric by the Kubelka-Munk Equation (Eq. 1).

$$K/S = \frac{(1-R)^2}{2R} \quad (1)$$

where $K$ is the absorption coefficient of the substrate, $S$ is the scattering coefficient of the substrate and $R$ is the reflectance of the dyed fabric at $\lambda_{max}$.

Color transfer rate was calculated by Eq. 2.

$$C_t(\%) = \frac{(K/S)_a}{(K/S)_b} \quad (2)$$

where $C_t$ is the color transfer rate, $(K/S)_b$ and $(K/S)_a$ are color yields of the sample washed before and after, respectively.

## 3. Results and discussion

### 3.1. Preparation of color polymeric nanomaterials by sunflower oil synergy

Disperse dyes are usually organic molecules that do not dissolve water. As our earlier studies have shown, there are multiple intermolecular and intramolecular forces between the dye molecules [24]. It is very difficult that the dyes are dispersed into the nanoparticles by mechanical means. However, the nanoscale particles for digital inkjet printing have a series of attractive properties and arouse wide interest [25,26].