# A Laser-Imageable Thin Coating Derived from Polymer Nano-particles Containing Infrared Dye [a]

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## Abstract

*This study is focused on a water-born thermo-sensitive material composition based on an infrared (IR)-sensitive (830nm) polymer nano-particles and the potentiality in preparation of environment-friendly CTP plate. Polymer nano-particles containing IR-absorbing dye (IR nano-particles) were prepared through soapless emulsion polymerization in the presence of active emulsifier and a redox initiation system. A water soluble polymer, poly (N-hydroxymethyl acrylamide) (PHMA), was used as the binder resin. An IR laser-imageable coating was prepared with the above materials as the main components. Upon laser exposure, the IR dye of the polymer particles absorbed IR energy and produced high temperature, leading the particles to be fused and causing great changes in both surface morphology and inner structure of the coating. As a result, the exposed areas were no longer water-soluble or water-dispersible, whereas the unexposed areas remained unchanged and were still soluble or dispersible in water. When developing with water, negative images would be obtained.*

## Introduction

Computer to plate (CTP) is an imaging technology used in modern printing processes. It has several advantages, e.g., filmless, high speed and high quality. CTP plates are the necessary consumption materials for CTP technology, and thermal CTP plates have been and will remain to be the major solution. Nowadays more and more customers switch to computer-to-plate technology. Since 2006, the starting year of the 11th Five Year Plan, until 2011, CTP plates consumed in mainland of China increased, on average, at 67.9% on an annual basis and about 150 million meters of CTP plate were consumed in 2012, which was roughly equal to that of consumed PS plate[1, 2]. However, most CTP plates currently used require wet processing using aqueous alkaline. To meet the increasingly stringent environmental requirements, chemical-free or processless CTP plate techology, which considerably reduce or eliminate the need for toxic organic solvents or chemicals, attracts more and more attentions. Most neutral water processable CTP plate coatings involved chemical reactions, which were either induced by light or acid or other stimulus during the imaging and follow-up processes [3]. Recently, Agfa has developed a new plate system based on thermo-fusable plastic particles, and the image formation is a simple physical process [4]. This research proposed an approach to a thermo-sensitive coating which consisted of IR-dye imbedded latex nano-particle and aqueous soluble binder resin. Upon laser exposure, high temperature caused the emulsion particles to be fused and polymer of the emulsion particle would meet and reach with the binder polymer. Both fusing and chemical reaction would contribute to generate high image contrast. In this paper, polymer nano-particles incorporated with infrared-absorbing dye were prepared and characterized. Preliminary works were also done to prepare a thermo-sensitive water-developable latex coating and investigate the imaging performance.

## Experimental

### Materials and methods

3-Hydroxypropyl methacrylate (HPMA), methyl methacrylate (MMA), butyl methacrylate (BMA), L-ascorbic acid (LAA), vanadium (IV) oxide sulfate (VOSO4), hexadecanol and infrared absorbing dye (IR830) with the maximum absorption at 830 nm were commercial products from Beijing Chemicals Co. tert-Butyl hydroperoxide (solution 70% in water) (TBH) was purchased from Acros Organics and used as received. Polymerizable surfactant, SE-10N (Adekareasoap, Japan) was a commercial product and used without further purification. FC4430 was a commercial surfactant used as wetting and leveling agent for the water-born latex coating. Poly (N-hydroxymethyl acrylamide ) (PHMA) was prepared in our laboratory.

Ultraviolet-visible (UV-Vis) spectra were recorded on a UV-2501PC spectrophotometer at room temperature. The average particle size of the emulsion was measured by transmission electron microscopy (TEM) with a H-7000 apparatus (Hitachi, Japan). Differential scanning calorimetry (DSC) and thermo-gravimetric analysis (TGA) were recorded on a Netzsch DSC200PC analysis apparatus and a Netzsch TG209C instrument (heating rate: 10 oC/min), respectively. High pressure homogenization was performed on a NS3006L equipment (NIRO-SAOVI, Italia) at a pressure of 1500 bar. Film thickness was measured with a FTS-S3c ultra surface analysis instrument (Taylor Hbson Ltd., England). Laser imaging process was performed on a RCTP-1S laser (830 nm) imaging apparatus.

### Preparation of the IR nano-particles

IR830 (0.75 g) and hexadecanol (0.15 g) was dissolved in a mixture of HPMA (10.0 g), MMA (15.0 g) and BMA (5.0 g). SE-10N (1.60 g) was dissolved in 90 ml of water. The IR830-monomer mixture was added drop-wise into the SE-10N water solution under constant stirring, which was then treated with a high pressure homogenizer. The emulsion obtained after high pressure homogenization was placed in a four-necked flask and mechanically stirred for 1 h at 25 $^{o}$C under nitrogen atmosphere. 10 ml of aqueous solution of LAA (1.25 g) in water was added to the mixture. The temperature was raised to 28-30 $^{o}$C. Then, t-BHP/ $VOSO_4$ (1.1 g/10 mg) aqueous solution (20 ml of water) was added dropwise to the above emulsion with a peristaltic pump under continuous nitrogen flow and mechanic stirring. The feeding rate was set at 0.6 ml/min. After the addition (within 50 min), the emulsion was stirred for another 5 h. Finally, the IR dye-containing poly(HPMA - MMA - BMA) emulsion was filtered with a Buchner funnel. The filtrate was collected and kept for later use. The solid particles were obtained with the above emulsion by precipitation in aqueous ethanol (50 wt.%), centrifugation, filtration, washing with water and then dried at 40 °C in vacuo overnight.

### Preparation of the latex coating derived from the IR nano-particles

PHMA water solution (1.2 g, 20 wt.%) and 1.0 wt.% FC4430 water solution (3 drops) were successively added to the prepared the polymer emulsion (12.0g, 22 wt.%) under magnetic stirring. The mixture was spin-coated on a clean aluminum plate (a 0.3 mm thick aluminum substrate with electro-grained and anodized surface), and then dried at 60 °C in an open oven for 10 min. Coating thickness of 1.6-1.8 g/m$^2$ was obtained by carefully adjusting the spin rate. For imaging, the sample plate with a thin coating was mounted on the exposure device for laser scanning and then developed with neutral water at 25 °C. The surface topography was recorded with an optical microscope.

## Results and Discussion

### Preparation of the IR nano-particles

Through mini-emulsion polymerization of the IR830-monomers (i.e., HPMA, MMA and BMA) mixture, poly(HPMA-MMA-BMA) nano-particles were prepared [5]. SE-10N and hexadecanol were used as the reactive emulsifier and co-emulsifier, respectively. The co-emulsifier serves to reduce the average size of the polymer particles. High pressure homogenization is also necessary for obtaining nanometer-sized emulsion particles.

A redox initiating system was used to conduct the emulsion polymerization process. With the addition of t-BHP/VOSO$_4$ aqueous solution, the emulsion polymerization was started. It should be noted that the IR dye is sensitive to oxidants such as t-BHP, which will soon cause color change of IR830. On the other hand, IR830 is fairly stable in acid environment. Therefore ascorbic acid was firstly mixed with the pre-emulsion of IR830-monomer mixture and TBH was slowly added to avoid excessive oxidant in the reaction mixture. The free radicals generated in the aqueous phase diffused into the droplets and initiated polymerization. With the progress of the polymerization, the temperature of the reaction mixture gradually increased from 30 °C to as high as 45 °C within 25 min and then gradually dropped. The color of the reaction mixture deepened and finally turned into dark green. The emulsion was quite stable narrowly distributed in particle size. According to the TEM (Figure 1), the average size of the polymer particles was about 50 nm in diameter.

The UV-Vis spectrum of the prepared emulsion was shown in Figure 2. As seen, the emulsion of the IR830-containing polymer particles exhibits a maximum absorption at approximately 830 nm, which is almost the same as that of IR830. This indicates that IR830 was successfully incorporated into the polymer particles and the chemical structure remained stable during the emulsion polymerization. Thus, the prepared nano-emulsion can be used to prepare a water-born IR (830 nm) -sensitive information recording material, in which the IR830-containing nano-particles act as the active IR laser-absorbing component and heat producer.

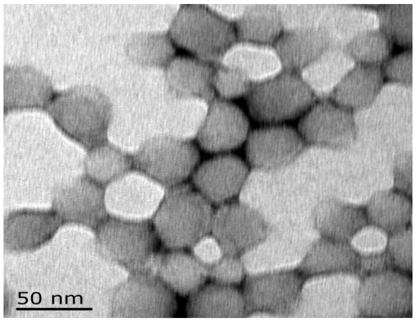

*Figure 1. TEM photographs of the IR830-containing nano-particles*

### Thermal analysis of the IR dye-containing polymer nano-particles

Thermal properties of the emulsion particles were measured by DSC (Figure 3) and TGA (Figure 4). The DSC result of the IR dye-containing polymer nano-particles. As seen, there is a small exothermal peak around 75 °C, which is assigned to the glass transition temperature of poly(HPMA-MMA-BMA) of the emulsion particles. For this reason, the processing temperature of the latex coating based on the IR dye-containing polymer nano-particles should not be higher than 70 °C, or else the particles the polymer particles cannot retain the form and structure during the coating preparation. Suitably low glass transition or melting temperature is very important to the present coating system in terms of laser induced fusing imaging. In this study, the latex thin coating was dried at 60 °C (about 12 °C lower than the glass transition temperature). The endothermic peak starting at about 270 °C is ascribed to the thermolysis of the polymer. As seen in Figure 4, little weight loss (< 2%) is detected for the solid IR nano-particles until the temperature was raised to 225 °C, and temperature at 5% weight loss was near 270 °C. This is in agreement with the DSC result.

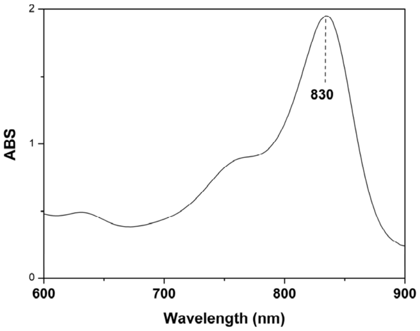

*Figure 2. UV-Vis spectrum of the IR830-containing polymer particles*

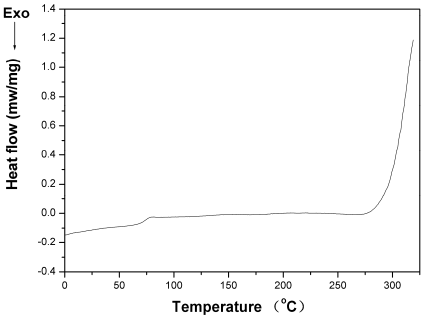

*Figure 3. DSC result for the polymer nano-particles*

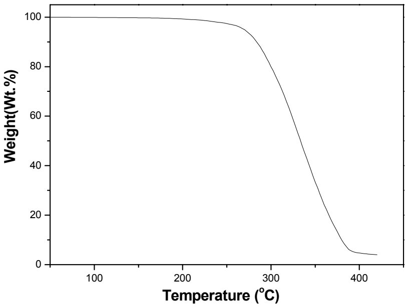

*Figure 4. TGA result for the polymer nano-particles*

### *A preliminary study on the imaging performance of the coating derived from the IR nano-particles*

The thin coating contained the following principal constituents: the prepared polymer nano-particles and PHMA (binder resin). Because the nano-particles had a very hydrophilic surface and PHMA was a highly aqueous soluble polymer, the prepared coating was hydrophilic and could be easily redispersed in neutral water. However, when exposed to IR laser, the IR dye-containing nano-particles in the exposed area would be fused and the boundary between particles and porous structure of the coating disappeared. Because the latex polymer together with the IR dye comprised the majority (about 85 %) of the coating, the hydrophobic components from the latex formed the continuous phase of the imaged areas. Thus, the imaged areas should become hydrophobic and resistant to water, and remained on the substrate after development. On the other hand, the unexposed areas of the latex coating still remained hydrophilic and could be easily removed from substrate with water during the development. Figure 5 shows the laser imaging process.

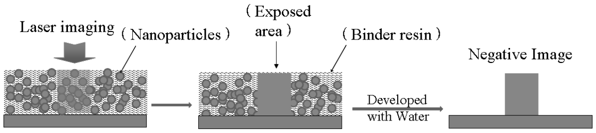

*Figure 5. Laser imaging of the coating*

*Figure 6. Micrograph of the exposure image after water developing (25 oC)*

## Conclusions

Oil-soluble IR dye was successfully incorporated into narrowly distributed polymer nano-particles via soapless emulsion polymerization. The polymer nano-particles exhibited a maximum absorption near 830 nm and were sensitive to 830 nm laser radiation. The coating derived from the IR nano-particle is laser-imageable and can be developed with water, which might be applied in developing environment friendly CTP plate.

## References

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## Author Biography

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