A Modified Phenolic Resin and its Effectiveness as Polymer Binder in Thermo-Sensitive Imaging Composition [a]

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Abstract

The performances of CTP plate depend heavily on polymer binder and those capable of producing large image contrast by exposure are keys to quality plate. This research proposed a polymer resin containing hydrophilic spices in the side chain which could be sheltered by the thermal induced crosslinking reaction during plate manufacturing process and released upon imaging exposure. The resin was prepared through esterification reaction of maleic anhydride with phenolic resin, and its chemical structure was characterized by IR spectrum. Plate coatings were formulated with the modified polymer as binder resin, 2,2-bis(4-(2-(vinyloxy)ethoxy)phenyl)propane as the crosslinking agent, a near infrared absorbing dye and crystal violet as the tracing agent. Solubility of the exposed and unexposed coatings in diluted aqueous alkaline was investigated in situ using a home-made dissolving rate tester. It was found that polymer containing 4-6% mole carboxyl groups led to high image contrast and this contribution came directly from the cross-linking and decrosslinking reactions. Preliminary test indicated that this polymer coating generated positive image of high contrast after exposure and could be used as CTP plate coating for thermal laser imaging.

Introduction

Computer-to-plate (CTP) technology has become the mainstream of printing industry due to several advantages, such as high sharpness, increased plate production outputs, more consistent, repeatability and so on. Much effort has been devoted for developing CTP plates, among which thermal plates seem to be the major direction [1]. Thermal plates have unique characteristics: high quality, more accurate plate registration, reproduction of a greater tone range, smaller dot gain and more thick printing ink layer [2,3]. However, there still exist some problems with most currently used CTP plates (at least in china), such as low developing tolerance, instability of imaging performance and so on. To a great extent, these problems are the inherent problems of thermal CTP's imaging mechanism - thermally induced variations of the molecular aggregates and intermolecular physical interactions, which are not great enough to provide sufficient solubility differential between the exposed and unexposed areas. Based on this background, a lot of work still needs to be done to overcome the shortcomings [4-6].

In our previous work, we found that divinyl ether was very reactive with carboxylic acid at suitable temperatures (typically 80-120 °C) and could be an effective cross-linker for polymers with pendant carboxyl group [6]. The bridging mechanism is the formation of acetal ester bond between the polymer chains through the reaction of carboxyl group with the divinyl ether group. However, this acetal ester bond could be readily cleaved at high temperatures (around 180 °C) in the presence of strong acids. As a result, the molecular weight becomes decreased together with the release of carboxy groups which greatly contribute to the solubility increase of the imaging layer in developing solution, therefore a great contrast could be observed after heat treatment. These features allow us to develop a thermo-sensitive material with good combined properties.

Phenolic resins and derivatives exhibit excellent combined properties and are widely used as matrix resin in imaging compositions of printing plates [7]. In this paper, a modified phenolic resin bearing side carboxy groups was synthesized. Thermo-sensitive image formation layers consisted of the modified phenolic resin, an IR-sensitive dye, a divinyl ether and an acid generator were prepared and studied. Laser imaging exposure was also conducted to test the imaging performance.

Experimental

Reagents and Methods

Phenolic resin (Mn = 5000, maleic anhydride, 2-methyl-4,6-bis(trichloromethyl)- 1,3,5-triazine (MBTT) and infrared sensitizing dye with a maximal absorption at 830 nm were purchased from Beijing Chemical Reagents Company. 2,2-Bis(4 -(2- (vinyloxy)- ethoxy) phenyl)- propane (BVPPP) was prepared according to the reported procedure [8]. Other reagents and solvents were commercial products and were purified before use.

IR spectra were measured with a Shimadzu FTIR-8400 spectrophotometer. Laser imaging was performed on a RCTP-1S laser apparatus (830 nm, China). Determination of dissolving rate of the resin coatings in alkaline solution (10% $NaSiO_3$ aqueous solution) was conducted on a home-made device, which consists of a UV-Vis. spectral photometer, a special sample chamber and a solution supplying system [6]. The device can on-line detect the ABS value of the coating in a selected solution, which reflects the changing of the coating thickness. The photometer was set in ABS~time mode and ABS/(ε×C) was plotted against time, where ε and C were molar extinction coefficient and concentration of the indicator, respectively. Since ε and C were kept constant in this study, ABS or ABS/(ε×C) were linearly correlated to coating thickness according to Beer-Lambert Law. Optical micrograph was recorded on a VHX-600 microscope.

Esterification of the Phenolic Resin

Phenolic resin (10.6 g), maleic anhydride (0.49 g, 5 mmol) and 1,4-dioxane (25 ml) were placed in a 250-ml, three-necked flask equipped with a mechanical stirrer and a reflux condenser. The mixture was refluxed with stirring for 10 h. Then, the organic solvent in the mixture were removed with a rotary evaporator to give the yellowish solid product.

Resin Coatings Based on the Esterified Phenolic Resin and BVPP

Four coatings were prepared by applying three different levels of BVPP. Esterified phenolic resin (2.0 g), BVPP (0.0 g, 0.18 g, 0.36 g and 0.54 g), MBTT (0.1 g) and infrared sensitizing dye （0.07 g） were dissolved in 8 ml of 1,4-dioxane to give a clear solution, which was then spin-casted onto a glass plate (or aluminum substrate) and heated (80 oC/10 min and 100 oC/10 min) to obtain the resin coatings. Finally, the dissolving dynamics of the polymer coatings was measured and compared under identical experimental conditions.

The sample coatings were mounted on the rotating disc of the exposure device for laser scanning. Finally, the exposed coating was developed with 10 % NaSiO3 aqueous solution for 25 s at 25 oC and the image was detected by microscope.

Results and Discussion

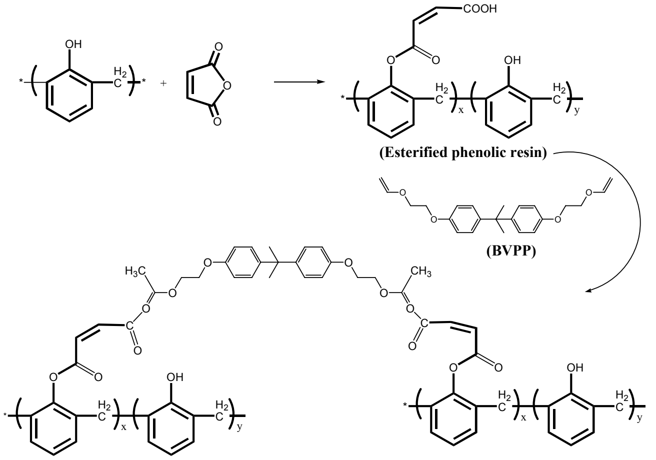
Preparation of the Esterified Phenolic Resin and the Resin Coatings

A modified phenolic containing carboxy groups was synthesized through the reaction of phenolic resin with maleic anhydride (Scheme 1). Figure 1 compares the IR spectra of the phenolic resin (curve a) and the obtained esterified phenolic resin (curve b). Compared with curve a, there appeared a strong absorption at 1720 cm-1 which is ascribed to the characteristic absorption of the newly-formed ester groups.

Resin coatings were prepared from the solutions of the esterified phenolic resin, BVPP, MBTT and the infrared sensitizing dye. The components played different roles: the esterified phenolic resin was the matrix resin and BVPP acted as the chain-extending agent; MBTT was an acid-generating reagent at high temperatures (>180 oC); the infrared sensitizing dye is a light-to-heat conversion material, which absorbs IR radiation and transforms the IR energy into heat efficiently. It is also a coloring agent for the determination of the dissolution characteristic of the resin coatings.

As shown in Scheme 1, the carboxy group of the modified phenolic resin reacted with the vinyl group of BVPP to afford extended molecular chain during the drying process of the coating formation. Other things being equal, four coatings with different contents of BVPP were made in order to investigate the effect of BVPP on the chain-extension reaction. The coatings were denoted as C-1 (BVPP-free), C-2 (0.18 g of BVPP), C-3 (0.36 g of BVPP) and C-4 (0.54 g of BVPP). In order to facilitate comparison, the phenolic resin coating (C-5) was also made according to the above procedure for C-1, except that the esterified phenolic resin was replaced by the phenolic resin. Cure c is for the resin coating 2, which is almost identical to curve b. The characteristic absorption peak of the ester group remained the same, indicating that the ester group was stable in the coating-forming process. Strong absorptions in the range 1450-1630 cm-1 were observed in all the three curves, which were attributed to the aromatic rings.

Evaluation of dissolving dynamics of the resin coatings



Scheme 1. Esterification of the phenolic resin and the chain extension reaction during the coating-forming process

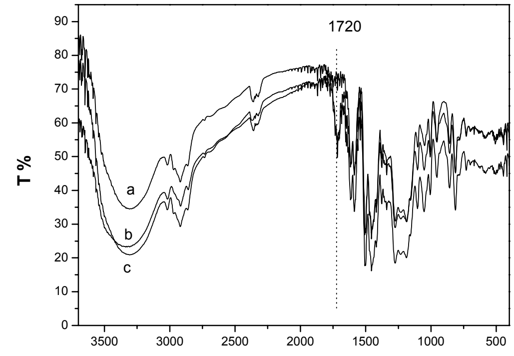


Figure 1. FT-IR spectra of the phenolic resin (a), the esterified phenolic resin (b) and the resin coating made from esterified phenolic resin (C-2)

It is reasonable that the esterified phenolic resin should have higher dissolution rate in alkaline solutions than the starting phenolic resin due to the incorporation of polar carboxy groups. However, in case the carboxy groups are reacted with BVPP and converted to acetal ester bonds (Scheme 1), not only the polarity of the resulted polymer gets lower but also the molecular weight becomes higher. With the combination of these two factors, the dissolving capacity of the chain-extended resin coatings should have reduced solubility.

The dissolution behaviors of the resin coatings were determined by on-line tracing the coating thickness change in 10% NaSiO3 aqueous solution. According to the Beer-Lamber law, the coating thickness is in direct proportion to the ABS value. As seen in Figure 2, the ABS value is shown on the vertical axis and time (s) on the horizontal. It is clear that the dissolving behaviors of the coatings are different. The coatings can be sorted by dissolution rate in the following order: C-1 >> C-2, C-5 > C-3 > C-4. The complete dissolution times were about 33 s, 77 s, 69 s, 87 s and > 80 s for C-1, C-2, C-3, C-4 and C-5, respectively. This might be explained by that the coatings had different molecular structures and molecular weights. C-1 contained the esterified phenolic resin in which about 5% of the phenolic hydroxyl groups had been esterified and thus converted into the carboxy groups. The carboxy groups made C-1 more soluble than C-5 (derived from the starting phenolic resin) in alkaline solution. This corresponds to anticipation. As for C-2, C-3 and C-4, the influenced factors are more complex. In the preparation process of the three coatings, chemical reactions occurred between the carboxy groups and the vinyl groups. If the conversion rate of the carboxyl group is high enough, the resin coating should become quite difficult to dissolve. The molar ratios of the vinyl group of BVPP to the carboxy group of the esterified phenolic resin were 1:1, 2:1 and 3:1 for C-2, C-3 and C-4, respectively. It is certain that excessive addition of BVPP (chain-extending agent) facilitate the conversion of carboxy group and the molecular weight increase. Therefore C-4 exhibited excellent resistance to the alkaline solution，and C-3 was just inferior to C-4. There is no big difference between C-2 and C-5, though the former had extended molecular chain structure. The possible reason is below: some carboxyl groups remained in the C-2 coating due to low dose of BVPP and this counteracted the effect of the chain extension.

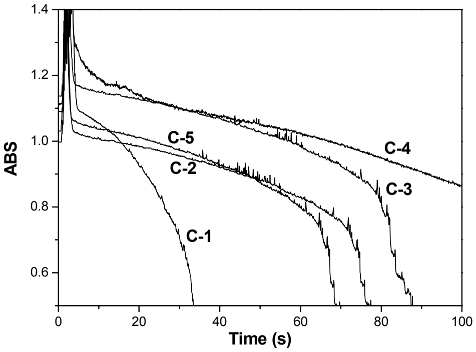
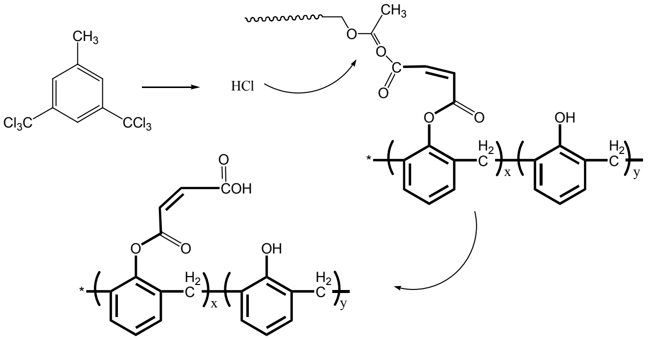


Figure 2. Dissolving dynamic curves of the resin coatings



Scheme 2. Laser imaging exposure induced decomposition of the resin coatings

Laser imaging of the resin coatings

IR laser imaging was performed to get an elementary knowledge of the effectiveness of the resin coatings as thermo-sensitive compositions. The imaging energy was fixed at 120 mJ/cm^2. When the resin coatings were exposed to IR laser exposure, the temperature of the exposed area was increased sharply, causing the thermolysis of MBTT (the acid-generating agent) to release hydrochloric acid, and this further induced the polymers in the exposed area decomposed. In this stage, the relatively weak acetal ester bonds might be broken down and carboxy groups would be released (Scheme 2). As a result, the exposed areas should have improved solubility in developer, which contributed to the solubility differential between the exposed and unexposed areas. This might make it possible to generate a good image after development.

After laser imaging exposure, the resin coatings were then developed (in 10% $NaSiO_3$ water solution) and rinsed to provide negative images. Figure 3 is a micrograph of the patterns of the resin coatings which were exposed by IR laser, followed by development for 25 s at 25 °C. The grey areas are the surface of the aluminum substrate (the exposed areas); the dark areas or lines are the unexposed area. For C-3 (Figure 3C) and C-4 (Figure 3D), the resin coatings in the exposed area was completely washed out by developer, while that of the unexposed area still remained on the substrate, showing clearly developed image and clear background of the substrate. However, in the case of C-2 (Figure 3A) and C-5 (Figure 3B), some unexposed areas were removed by the developer to give poor exposure image. This showed that the resin coatings of C-2 and C-3 were less resist to the developer under the experimental conditions. As discussed above, some of the carboxy groups remained in C-2 caused the coating to be less resistant to the developer despite that chain-extending reaction occurred in the coating formation. Nevertheless, C-3 and C-4 exhibited acceptable imaging performance, showing the effectiveness of the image formation material based on the esterified phenolic resin, BVPP and MBTT.

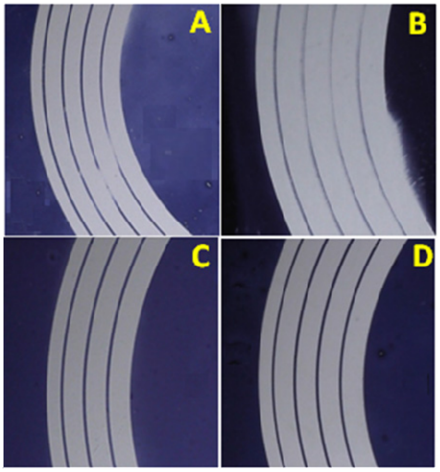


Figure 3. Micrograph of the resin coatings (A/C-2, B/C-5, C/C-3, D/C-4) after IR laser exposure, followed by wet development process (50 times)

Conclusions

An esterified phenolic resin containing carboxy groups was prepared and applied in the thermo-sensitive image formation coatings based on chain-extension and thermal-degradation mechanism. Investigations on the dissolving dynamics and laser imaging performance of the resin coatings show that the chain-extending process in the coating formation process is a key step and needs further optimization in the future work.

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Author Biography

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