The Synthesis and Application of Dye-Fixing Agents with Different Properties

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Abstract: The monomer concentration and initiator amount have significant impact on the synthesis of dimethyl diallyl ammonium chloride (DMDAAC) process, when these two variables are adjusted, the molecular weight and cationic degree of PDMDAAC will be also changed. In this paper, PDMDAAC with different properties were obtained by changing the above conditions. Different PDMDAAC was added to the Inkjet coating paper as dye-fixing agent respectively and the effects of them on improving the Ink-jet printability were analyzed comparatively. The results showed that PDMDAAC could improve the printing properties of ink-jet printing papers. The preferable molecular weight of PDMDAAC was about 100,000 and the charge density was about 5mmol/g.

Keywords: PDMDAAC; Inkjet Printing Paper; Printability

1. Introduction

Dimethyl diallyl ammonium chloride (DMDAAC) is the kind of quaternary ammonium with two unsaturated bonds the homopolymer and copolymer of which have high density positive charge, good water solubility and easily controlled molecular weight. Dimethyl diallyl ammonium chloride (DMDAAC) polymers are cationic polyelectrolytes which are used in dealing with industrial wastewater, domestic sewage and potable water, mining, oil exploitation, printing and dyeing. Therefore, PDMDAAC is an extremely promising cationic polymerization material and has become a very active subject in the world [1]. In this work, the synthesis of DMDAAC homopolymer and the effects of the PDMDAAC with different properties used as dye-fixing agent on coated inkjet printability were studied.

2. Experimental

2.1. Synthesis

2.1.1 Materials

Chemicals: dimethyl diallyl ammonium chloride, ammonium persulfate, EDTA-4Na.

Experimental apparatus: thermostatic water bath, Ubbelohde viscosity meter, particle charge detector of Germany Wlek Analytic Gmbh, FTIR-650.

2.1.2 Methods

The stirrer, condenser pipe and three-neck flask with airway tube were placed in thermostatic water bath. After adding a certain concentration of DMDAAC solution, nitrogen was flowed about 20 minutes in order to remove the soluble oxygen and then a certain amount of the chelating agent Na_4EDTA of 0.01g/mL and a certain amount of the initiator $(NH_4)_2S_2O_8$ of 0.1g/mL (APS) were added. The key synthesis factors are reaction temperature and time, under appropriate conditions the colorless, transparent and syrupy liquid can be obtained [2] [3].

The influence of reaction temperature and time to polymer was regulated and the monomer conversion, molecular weight and charge density were detected [4]. The infrared attribute to Poly dimethyl diallyl ammonium chloride was also carried out.

2.2. Coating

2.2.1 Materials

Base paper: An uncoated paper with a base weight of 80g/m^2 was used as the main substrate for the coating.

Pigments: 507E aerosil with the average particle size 7μm, specific surface 252.1m^2/g, pore volume 1.7-1.8ml/g and whiteness ≥ 85% from Shanxi Tianyi Nano Material Technology Co., Ltd.

Adhesive: PVA1788 with alcoholysis degree of 86.0 ~ 90.0%

2.2.2 Methods

The adhesive and dye-fixing agents were added to pigments disperse solution. When the mixture was well-distributed, the base paper could be coated. The dosage of adhesive was 20% of pigments and solid content was 24%. The amount of PDMDAAC contained in the coating was 0.5%, and the gap of scraper was 0.10mm. Then all coated sheets were calendered for their post-drying [5] [6].

3. Results and discussion

3.1. The effect of monomer concentration on polymerization reaction

The dosage of chelating agent Na_4EDTA and initiator $(NH_4)_2S_2O_8$ was 0.01% and 0.5% on o.d. monomer respectively. The characteristics of polymers under the condition of different monomer concentration were showed in Table 1.

Table 1. The effect of monomer concentration on the polymerization reaction

Monomer concentration/%	Conversion/%	[η]	Molecular weight($\times 10^4$)	Cationic degree
30	60.1	0.58	3.88	3.04
35	66.3	0.73	5.14	3.89
40	70.5	0.91	6.73	4.78
45	77.8	1.31	10.49	5.12
50	85.3	1.42	11.58	5.89
55	87.3	1.99	17.48	5.99
60	88.7	2.27	20.51	6.12

Table 1 shows that with the increase of monomer concentration, the conversion rate and cationic degree increased steadily. Due the implosion occurs when the concentration was over 50% occasionally, So that deionized water was added in this synthesis process to prevent the implosion occurring.

3.2 The effect of initiator dosage on polymerization reaction

It can be seen in Table 2 that the conversion rate and cationic degree increased first and then decreased with the increase of initiator dosage. When the dosage of initiator was 0.5%, the conversion rate, cationic degree and molecular weight attained the biggest value. Therefore the optimal initiator dosage in the synthesis of PDMDAAC was 0.5%.

Table 2. The effect of initiator dosage on the polymerization reaction

Initiator dosage/%	Conversion/%	[η]	Molecular weight($\times 10^4$)	Cationic degree
0.3	55.1	0.68	4.72	3.64
0.4	66.3	0.76	5.40	4.09
0.5	77.8	1.31	10.49	5.12
0.6	67.8	0.91	6.73	4.78
0.7	55.3	0.83	6.01	4.32

3.3. The Fourier infrared spectrum analysis of PDMDAAC

The infrared spectrum of synthesis sample was showed in Figure 1. The ammonium salt [$-CH_2N + (CH_3)_2CH_2-$] absorption peak was near 970cm^{-1}. The N + methyl stretching vibration peak was near the 1421cm^{-1}, 1475 cm^{-1}. C-C stretching peak and the water peak were both near 1640 cm^{-1}. The C-H vibration peak related to double bonds was significantly reduced indicating that the unsaturated double bonds have been converted, but few residual monomers could not be effectively separated, there was still little absorption peak.

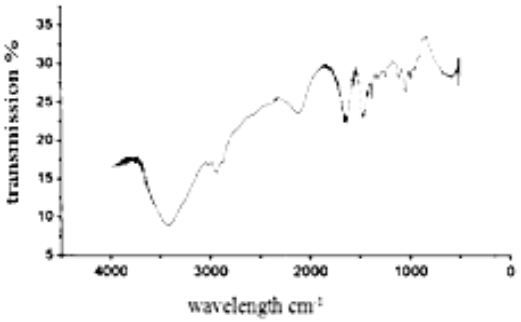

Figure 1. The Fourier infrared spectrum of PDMDAAC

3.4. The effect of PDMDAAC with different properties on printability

3.4.1 Color density

The higher color density means that the image is much brighter and the continuity of ink dot is much better. PDMDAAC with different properties was used as dye-fixing agent in the coating to improve the printability of inkjet paper.

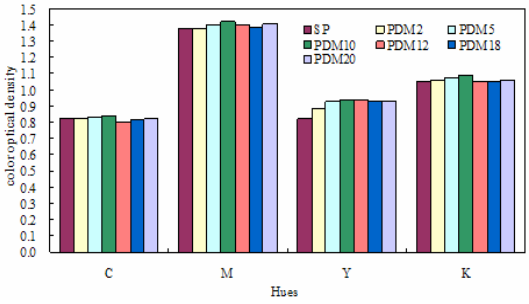

Figure 2. The effect of PDMDAAC on the color density

Note: SP – control sample (no dye-fixing agents PDMDAAC in the coating); PDM2 - molecular weight of 20,000; PDM5 - molecular weight of 50,000 and count analogically.

Due to dye-fixing effect of PDMDAAC on ink pigment which can prevent the ink permeating excessively, the color density of inkjet paper containing PDMDAAC was enhanced with different degree compared the con-

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trol sample SP. When the molecular weight was about 100,000, the color density of CMYK was improved 2.8%, 2.9%, 14.5% and 4.3% respectively. The improved degree sequence of color density was as follow: Y>K>M>C and the yellow ink could obtain the best effect. So the PDMDAAC can fasten the pigment and prevent the ink permeating excessively [7] [8].

3.4.2 Lines sharpness

For ink-jet printing, sharpness of images is related to the image pixel resolution, the printer resolution, paper resolving power and the image itself. The capillary in the surface of paper will cause the spread of printed lines. So the quality of the printed lines can be evaluated by comparing the roughness of horizontal and vertical lines.

CMYK four-colored horizontal and vertical lines with different width were measured by using the microscope and image analysis software Image Pro Plus6.0.The mean roughness of colored lines were shown in Table 3.

It can be seen in Table 3 that after adding fixative PDMDAAC, the clarity of the printed lines improved, the spread of ink reduced. The lower the molecular weight of PDMDAAC was, much more obvious the effect was.

Table 3. Mean roughness of vertical and horizontal CMYK lines (unit: μm)

Hue	SP	PDM2	PDM5	PDM10	PDM12	PDM18	PDM20
C	107	104	103	102	103	105	106
M	95	93	94	92	93	93	94
Y	110	109	102	103	109	107	108
K	98	93	92	91	98	93	92
Mean	102.5	99.7	97.7	97	100.7	99.5	100

3.4.3. Water resistance

When the image is wetted by water, the dye loss of printed image depends on the binding degree of dye and coating. Inkjet printing usually uses water-based ink, so water resistance of the image is essential. The density difference before and after wetting generally requires less than 0.25. In this experiment, the CMYK colorlumps were submerged in distilled water at 25°C for 1 minute at first, and then the density values were measured after drying and the density difference was calculated [9].

As can be seen from Figure 3, the water-resistance of sheets was significantly enhanced after adding fixing agent PDMDAAC. The cationic fixing agents can attract anionic dye molecules to the surface of silica pigments, so the pigments can be stabilized to improve the water resistance of ink spots. The better fixing agents were PDMDAAC with molecular weight 50,000 and 100,000.

3.4.4. Color difference

Reduction of color refers to the consistency of color inkjet printing paper and the original image in color. It is an important criterion for measuring the image quality of color inkjet paper. The values of L, a, b of colorlumps were measured by using CIELAB optical densitometer. The color reproduction was calculated according to 1976 color difference formula $\triangle E = (\triangle L^2 + \triangle a^2 + \triangle b^2)^{1/2}$. The less the color difference is, the lower the chromatic aberration is and the better is of the color reproduction of paper [8].

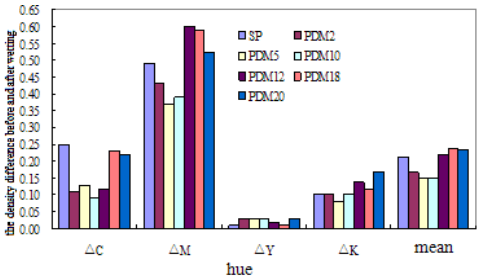

Figure 3. The effect of PDMDAAC on water resistance

In Figure 4, the color difference was significantly reduced after adding fixative PDMDAAC and color density, clarity were improved to some degree. Chromatic aberration was reduced to less than 4 NBS, paper color reduction performance was improved and the color was bright. Overall, when the coating was added with PDMDAAC, the chromatic aberration was the least, the color was closest to the original print and the reduction of various colors was much better.

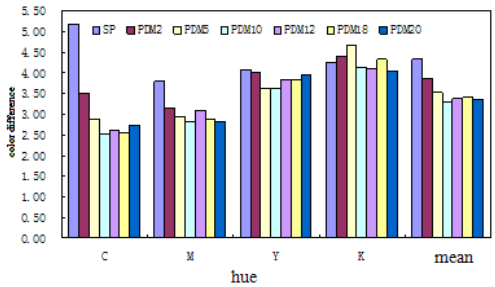

Figure 4. The effect of PDMDAAC on color difference (unit of ΔE is NBS)

4. Conclusion

Monomer concentration and the appropriate initiator dosage were essential factors in the synthesis of Poly dimethyl diallyl ammonium chloride (PDMDAAC). The requested polymers could be obtained by adjusting the concentration of monomer and initiator dosage.

Cationic fixing agent PDMDAAC could make a better fixation of anionic dye to the paper surface, reduce the infiltration and over-proliferation of ink, raise optical density of the printed image and improve the water-resistance. The optimal fixing agent to color ink-jet printing paper was PDMDAAC with molecular weight about 100,000 and the charge density of 5.12 mmol / g.

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